N. AKHMETOV, M. AZIZOVA and L. BADYGINA

Problems and Laboratory Experiments in Inorganic Chemistry

MIR PUBLISHERS • MOSCOW

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ИЗДАТЕЛЬСТВО
МИР

Н. С. АХМЕТОВ, М. К. АЗИЗОВА, Л. И. БАДЫГИНА

ЛАБОРАТОРНЫЕ И СЕМИНАРСКИЕ ЗАНЯТИЯ ПО НЕОРГАНИЧЕСКОЙ ХИМИИ

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА»
МОСКВА

N. AKHMETOV, M. AZIZOVA and L. BADYGINA

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PREFACE

th the content of general and inorganic chemistry and the odology of teaching have substantially changed during the past les. Basically, an entirely new course has been worked out. material is now discussed from the standpoint of modern con- in quantum mechanics, thermodynamics and the structure atter.

e course in practical general and inorganic chemistry must the same requirements. In our opinion this can be achieved igh exercises and laboratory experiments, which illustrate heory and stimulate the student to independent thought and i him how to apply theory to practical needs. The student must / how to handle chemicals properly and be able to perform atory experiments. Each experiment should be considered as dependent piece of research (at the level of the first year student) its own object, theoretical basis and experimental proof of onjectured result. The experiments must lead the student from perficial acquaintance with substances to an understanding of properties, thorough knowledge of their structure and thermo- mics, and further to the carrying out of an oriented experiment. is laboratory manual will, in our opinion, serve the purpose inging the teaching process closer to the solution of practical lems in chemical research.

his manual is the summation of our experience in teaching ral and inorganic chemistry at the Kazan Chemico-technological tute. The first part of the book is devoted to general theoretical lems in inorganic chemistry, while the second part to inorganic istry proper. The material is presented in such a way that all ents in a given subgroup can be characterized, while the experi- gained in examining the properties of one element can be exten- to the study of the other elements in the subgroup. The arrange-

ment of the material in the book facilitates the student in his independent studies.

The solution of difficult problems is given at the end of the book. Bibliographies will guide the student in his or her independent reading. The appendices will also considerably help students in their studies and in solving the problems given in this book. The data in the tables are taken from the cited literature.

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PART ONE

INTRODUCTION TO INORGANIC CHEMISTRY

I

THE STRUCTURE OF MATTER

CHAPTER 1

The Mendeleev Periodic System. The Structure of Atom

1. Formulate the main principles of quantum mechanics.
2. Calculate quantum energy of the radiation ΔE at wavelength of $\lambda = 300$ nm in joules; electron volts; joule/mole*.
3. Calculate the speed of an electron, a neutron or a particle having the mass of 1 g at which a de Broglie's wavelength is 0.1 nm.
4. Calculate the energy of the first five energy levels of an electron in the hydrogen atom and show their relative positions.
5. What is the principal quantum number of the hydrogen atom orbital if the electron energy is —3.4 eV; —13.6 eV; —0.85 eV, respectively?
6. What spectrum lines correspond to hydrogen emission as the electron passes from one energy state to another, the initial and final values of the principal quantum number being: $n = 4$ and 2; $n = 2$ and 1; $n = 3$ and 2?

To what region of the electromagnetic spectrum do these lines correspond?

7. Determine the energy of the electron transitions corresponding to the red ($\lambda = 656$ nm) and to the blue ($\lambda = 486$ nm) lines in the emission spectrum of atomic hydrogen.

Experiment 1. Observing the emission spectrum of atoms in a spectroscope. Fix a discharge tube filled with hydrogen (or helium, neon) in the vertical state in a stand and connect it to the ends of the secondary winding of the induction coil. Install a spectroscope so that its slit is at a short distance from the discharge tube and parallel to its capillary. Connect the induction coil to the D.C. source and switch on the current.

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* Data for calculations are given in the appendices.

Observe through the spectroscope a colourless flame of a gas burner. Put a piece of asbestos impregnated with a sodium chloride solution into the flame. Explain the yellow colour of the flame and the bright-yellow line in the spectrum.

Experiment 2. Observing the absorption spectrum of atoms. Using a spectroscope observe the emission of an incandescent electric lamp. Place a burner between the lamp and the slit of the spectroscope. Fix a piece of asbestos impregnated with sodium chloride solution in a stand and put it in the flame of a burner. Explain your observations.

Experiment 3. Observing the molecular spectrum. Proceed as in Experiment 1 and analyze the sulphur dioxide spectrum. Compare the spectra of the atom, molecule and solid (Experiment 2). What is the main difference between these spectra?

8. What energy changes in atom correspond to gamma-, X- and visible radiation?

9. Formulate the rules which define the number of orbitals and electrons in a given electron shell.

(a) What is the maximum capacity of electron shells K, L, M, N?

(b) What number of orbitals of a given shell is characterized by the following azimuthal quantum number: $l = 2$; $l = 1$; $l = 0$? What letters are used to designate orbitals?

(c) What number of electrons may be in the following energy states: $2s$; $4p$; $3d$; $5f$?

10. Characterize graphically the $1s$-state of the hydrogen atom electron using the following notions: (1) electron cloud; (2) boundary surface; (3) radial wave function; (4) radial probability density distribution; (5) radial probability distribution of finding an electron in an atom.

11. Characterize the $2p$-state of the hydrogen atom electron as in Problem 10.

12. Describe the form of the orbital and the electron cloud whose state is characterized by the following quantum numbers: $n = 3$, $l = 0$, $m_l = 0$; $n = 3$, $l = 1$, $m_l = 0, \pm 1$; $n = 3$, $l = 2$, $m_l = 0, \pm 1, \pm 2$. What symbols are used to designate orbitals?

13. What rules define the order of filling of the atomic shells? Give the electron configurations of unexcited atoms of Ge, Br, Mn, Ti and the ions Ba^{2+}, Fe^{3+}, Ce^{4+}.

14. Show graphically the variation of $4\pi r^2\psi^2$ with r for $3s$-, $3p$- and $3d$-states of the hydrogen atom electron. Explain the shape of the curves.

15. Plot a graph showing the variation of the orbital atomic radii with the atomic number for the elements of the 2nd and 3rd periods. Explain the shapes of the curve.

16. How does the value of the first ionization energy of atoms change with the atomic number of the element? Plot a graph showing the dependence $I_{ion} = f(Z)$ for the elements of the 2nd and 3rd periods. Explain the shape of the curve.

17. Compare the electron affinities of the nitrogen and oxygen atoms. Which of these atoms has a stronger electron affinity? Explain your answer.

18. Plot a graph of the variation of the first ionization energy of the atoms of alkali metals with the atomic number. Explain the shape of the curve.

19. Give the values of the first ionization energy of potassium, manganese and zinc atoms and their orbital atomic radii.

(a) How do the atomic radii change in the series K-Mn-Zn? Explain your answer (Fig. 1).

(b) How does the first ionization energy change in this series?

(c) Why is the first ionization energy of the rhenium atom (7.88 eV) higher than that of the manganese atom (7.44 eV)?

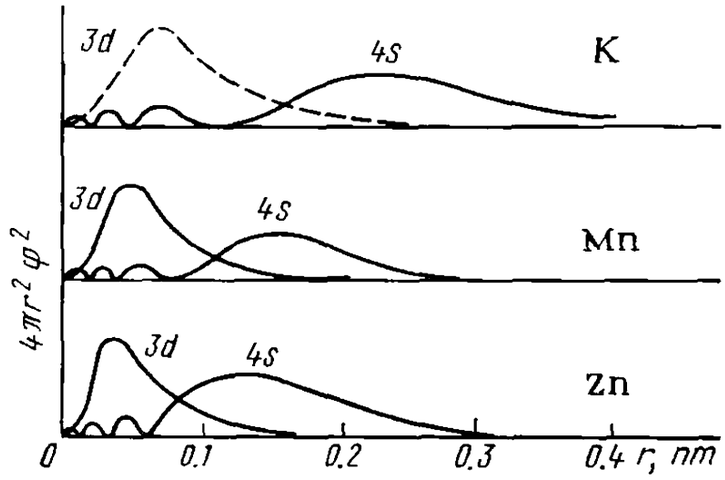


Fig. 1. Radial distribution of density of probability of finding electrons in the atoms of potassium, manganese and zinc

20. Show electron configurations of atoms of Group III elements in the ground state. What principle underlies the division of the elements of this group of the periodic system into subgroups?

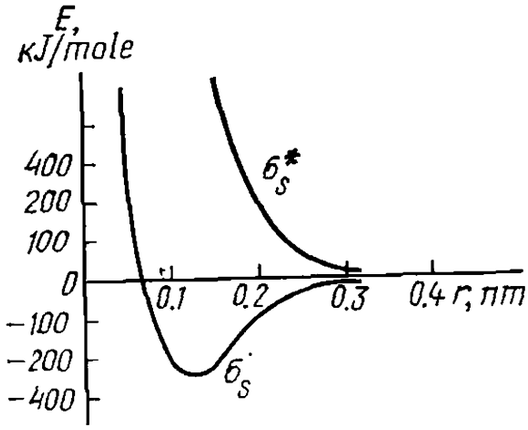


Fig. 2. Dependence of lowest energy levels of molecular hydrogen ion H_2^+ on the internuclear distance

CHAPTER 2

Chemical Bonding. The Structure of Molecule

2.1. Chemical Bonding

1. Formulate the main principles of the molecular orbital theory.

2. Figure 2 shows the lowest energy levels of the molecular hydrogen ion H_2^+ calculated with the Schrödinger equation by internuclear distance.

(a) What energy curve describes the H_2^+ ion in its ground state? How can the energy of dissociation of the molecular ion H_2^+ (to H and H^+) and the equilibrium internuclear distance be determined from the graph? What are the dissociation energy and internuclear distance of the ion H_2^+? (See Appendix 10.)

(b) Show graphically wave functions (along the axis connecting the nuclei) for the energy levels of the ion H_2^+ shown in Fig. 2.

(c) Draw the boundary surfaces and name the orbitals of the molecular ion H_2^+.

(d) Show graphically the variation of the probability of finding the electron in the bonding and antibonding orbitals of H_2^+ ion along the axis connecting the nuclei.

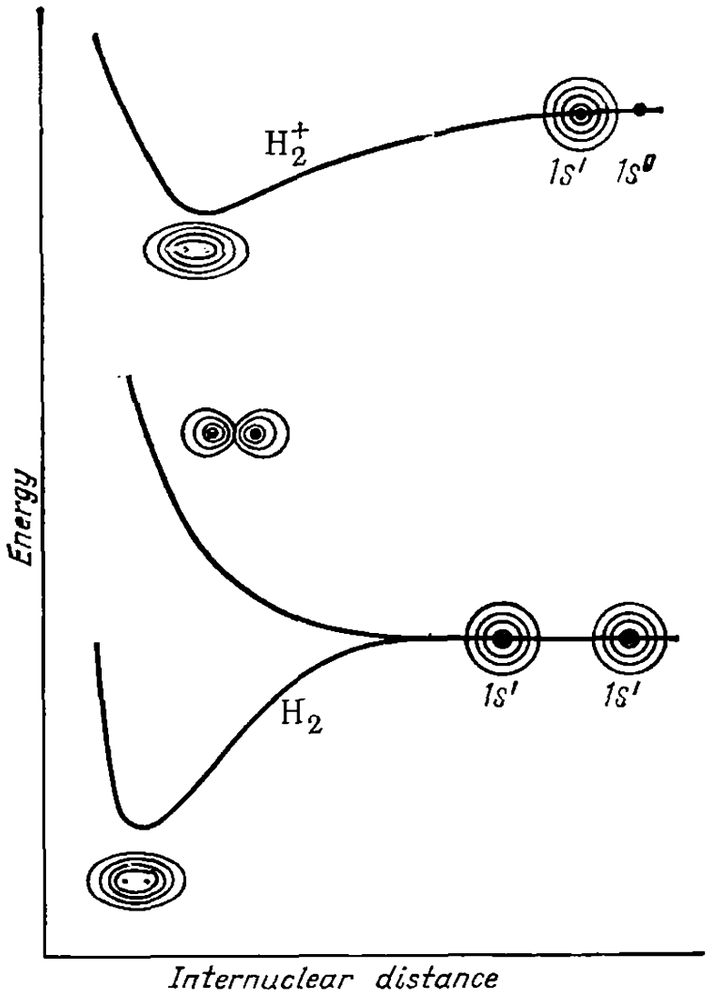


Fig. 3. Variation of potential energy of H_2 and H_2^+ with the internuclear distance

(e) Give the electron configuration of the H_2^+ ion in the ground state.

(f) Why do atoms combine into a molecule?

3. Formulate the main principles of the LCAO-MO method. How can the construction of the molecular orbitals from atomic orbitals be shown graphically for H_2^+ ion? What is the physical sense of such presentation?

4. Construct the energy diagram of the hydrogen molecule and distribute its electrons in the orbitals.

(a) Explain the difference between the ionization energies of the hydrogen molecule and the hydrogen atom in the ground state.

(b) Give the electron configurations of the ground and ionized (to H_2^+) states of the hydrogen molecule (Fig. 3).

(c) Using Fig. 3 explain the character of the variation of the energy of dissociation and the equilibrium internuclear distance with the hydrogen molecule ionization. Compare the dissociation energies and the internuclear distances of H_2 and H_2^+.

(d) Explain the difference in shape of the energy curves of H_2 and H_2^+ (Fig. 3) at the "bottom" of the energy well. In which case the bond is stronger, i.e. where higher energy is required to remove nuclei one from another to the same distance?

5. Show the overlapping in combinations of *s-s*-; *s-p*-; *p-p*-; *s-d*-; *p-d*-; *d-d*-orbitals.

(a) Indicate the cases of (1) positive, negative, zero; (2) σ-; π- and δ-overlapping (with respect to symmetry).

(b) What are the conditions for the formation of stable molecular orbitals from atomic orbitals?

6. Using the LCAO-MO method determine the number and the

shape of the fluorine molecule orbitals. Draw an approximate diagram of the energy levels of the molecule and give its electron configuration.

(a) What atomic orbital combinations are suitable (from the energy standpoint) for the formation of the fluorine molecule orbitals, if the $E_{2p} \gg E_{2s}$?

(b) What combinations of atomic orbitals lead to the formation of the molecular orbitals of the σ- and π-types if the axis connecting the fluorine atoms is the *z*-axis?

7. Determine the number and shape of the nitrogen molecule orbitals. Show graphically the approximate diagram of the energy levels of the molecule and give its electron configuration.

(a) What effect does the energy closeness of 2*s*- and 2*p*-orbitals of the atoms produce on the relative position of molecular orbitals on the energy diagram of homonuclear diatomic molecules?

(b) What is the bond order in the nitrogen molecule?

8. Draw the graph of the variation of the bond order, the force constant of bond *k*, its length and energy with the number of valency electrons in the series B_2-C_2-N_2-O_2-F_2-Ne_2

	B_2	C_2	N_2	O_2	F_2
k, N/m . . .	350	930	2240	1140	450

(a) Explain the curves.

(b) Which of these molecules are para- and diamagnetic molecules?

9. What is the character of the variation of the dissociation energy and internuclear distance in transition: (1) from N_2 to N_2^+ and N_2^-; (2) from O_2 to O_2^+ and O_2^-? Explain your answer.

10. Give the ionization energy of N_2 and O_2 molecules and N and O atoms. In what case is the molecular ionization energy higher (lower) than the atomic ionization energy? Explain.

11. Using the LCAO-MO method determine the number and the shape of the hydrogen fluoride molecule orbitals. Draw the approximate diagram of the energy levels of the molecule and give its electron configuration. The orbital energies of hydrogen and fluorine are

	1*s* (H)	1*s* (F)	2*s* (F)	2*p* (F)
E eV . . .	−13.6	∼−1000	−40	−17.4

(a) What combinations of the hydrogen and fluorine atom orbitals are most suitable for the formation of the molecular orbitals from the energy standpoint?

(b) What combinations of the hydrogen and fluorine atoms lead to the formation of the bonding, antibonding and nonbonding orbitals if the axis connecting the atoms in the HF molecule is the *z*-axis? Draw the diagrams of the orbital overlapping. What symbols are used to designate molecular orbitals?

(c) Why is the hydrogen fluoride molecule strongly polar? ($\mu = 0.64 \times 10^{-29}$ C·m, $\delta_F = 0.4-$).

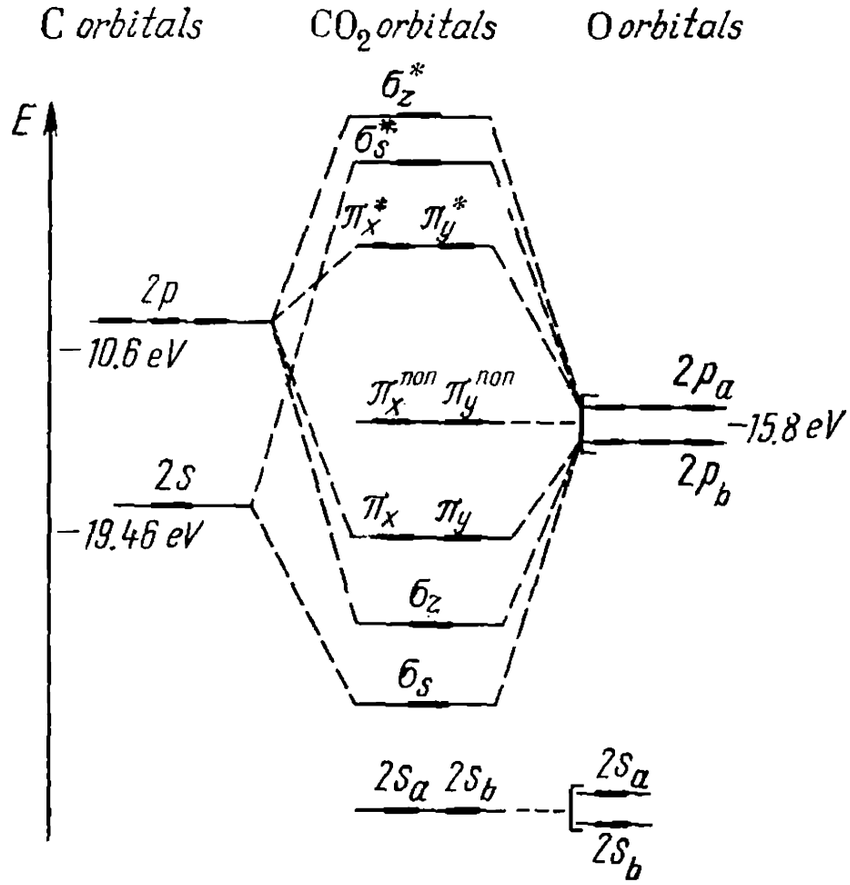


Fig. 4. Energy diagram of the orbitals of the linear molecule CO_2

12. Determine the number and the shape of the orbitals of a linear molecule of beryllium hydride, BeH_2. Draw the approximate diagram of the energy levels of the molecule and give its electron configuration.

(a) Why are the internuclear distances between Be and H in the BeH_2 molecule equal?

(b) How is the distribution of valency electrons in molecular orbitals coordinated with the positive effective charge on the beryllium atom ($\delta_{Be} = 1+$) and the negative charge on the hydrogen atom ($\delta_H = 0.5-$)?

13. Figure 4 shows an approximate diagram of the energy levels of the CO_2 linear molecule.

(a) What combinations of the central atom orbitals and group orbitals of peripheral atoms (ligands) are responsible for building molecular orbitals? Draw the overlapping diagrams.

(b) Explain the high mean energy ($E_{CO} = 803$ kJ/mole) and the force constant ($k = 1550$ N/m) of the bond CO and relatively short internuclear distance ($d_{CO} = 0.116$ nm) in the CO_2 molecule.

(c) Why is the bond in the CO_2 molecule polar while the molecule itself is nonpolar?

14. Determine the number and the shape of the molecular orbitals of a tetrahedral methane molecule. Draw an approximate diagram of the energy levels of the molecule and give its electronic configuration.

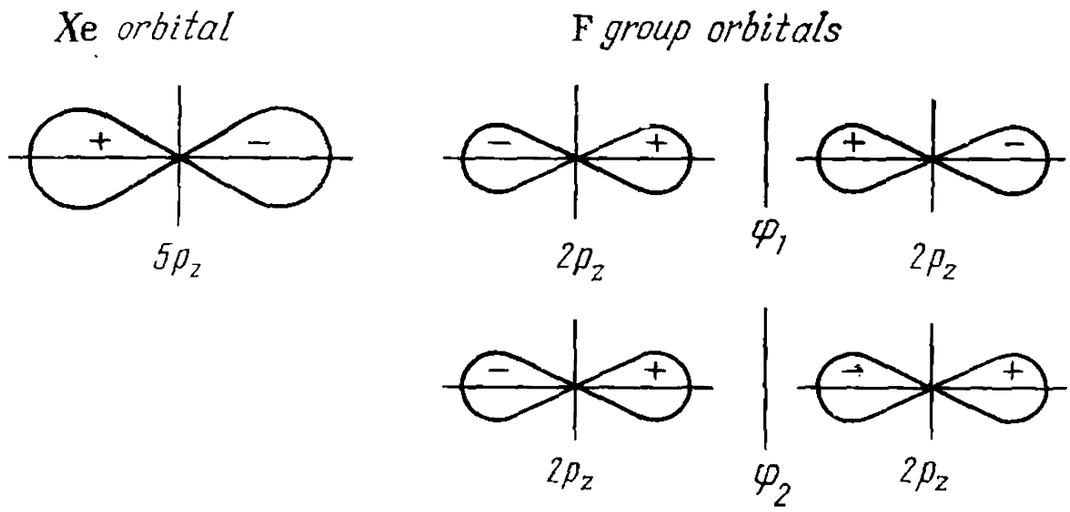


Fig. 5. $5p_z$-orbital of the Xe atom and group $2p_z$-orbitals of the atoms of the linear fragment F-Xe-F

(a) What combinations of the central atom orbitals and group orbitals are responsible for the formation of the molecular orbitals?

(b) Explain the equivalence of all four C—H bonds in the CH_4 molecule ($d_{CH} = 0.109$ nm).

(c) The ionization of the CH_4 molecule

$$CH_4 = CH_4^+ + e^-$$

occurs at two ionization potentials: 13.2 eV and 22.4 eV. Explain.

(d) What is the electron configuration of the tetrahedral ions BH_4^- and NH_4^+?

15. Compounds of crypton subgroup elements with fluorine and oxygen are known. These are, for example, KrF_2, XeF_2, XeF_4, XeF_6, XeO_3, etc. Formation of these compounds explains the existence of tricentre bonds. Thus, the orbitals of the linear molecule of XeF_2 are built at the expense of the combination of the $5p_z$-orbitals of the Xe atom (c.a) and group orbitals, consisting of two $2p_z$-orbitals of the F-atom (Fig. 5).

(a) Give the diagrams of overlapping of the central atom orbitals and group orbitals with the formation of the σ_z-, σ_z^* and σ_z^{non}-molecular orbitals.

(b) Give the diagrams of the energy distribution of the σ_z-, σ^{non}-, σ_z^*-orbitals of the XeF_2 molecule and locate valency electrons in the orbitals.

(c) What is the spatial configuration of the XeF_4 molecule assuming that it is composed of two perpendicular linear fragments of FXeF?

2.2. Valency. Oxidation State

16. (a) What is valency?

(b) What is the valency of the central atom (by the number of two-centre two-electron bonds) in the following compounds: BeH_2, CO_2, NH_4^+, BH_4^- (see Problems 12, 13, 14)?

17. (a) Define oxidation state.

(b) Determine oxidation states of the elements in the following compounds: $KMnO_4$, K_2MnO_4, K_2MnO_3, MnO_2, $K_2Cr_2O_7$, $K_3[FeF_6]$, $K[Al(OH)_4]$, $[Ni(NH_3)_6]Cl_2$.

18. Compare valencies, oxidation states and coordination numbers of the central atom in the following compounds: CO_2, NH_4^+, BH_4^-, BH_3, NF_4^+, BF_4^-, N_2.

2.3. Spatial Configuration of Molecules

19. (a) Formulate the main concepts of the model of localized electron pairs. Explain the spatial configuration of the molecule.

(b) Describe the spatial arrangement of two, three, four, five, six electron pairs around the central atom of the molecule.

(c) Determine the spatial configuration of CH_4, H_3N and H_2O molecules.

(d) Compare the bond angles of molecules and explain the variation in the series CH_4 (109.5°)-H_3N (107.3°)-H_2O (104.5°).

20. Using the models of localized electron pairs determine the spatial configuration of molecules: PF_5, SF_4, ClF_3, XeF_2, SF_6, ClF_5, XeF_4.

21. Explain the difference between the bond angles for the following pairs of molecules: OF_2 (103°) and H_2O (104.5°); NF_3 (102°) and H_3N (107.3°); NF_3 (102°) and PF_3 (104°).

22. (a) Formulate the main ideas of the model of hybridization of atomic orbitals for the explanation of the spatial configuration of molecules.

(b) Describe the spatial configuration of the *sp*-, sp^2-, and sp^3-hybrid orbitals around the central atom.

(c) What type of hybridization of the central atom orbitals is most probable for the molecules: CH_4, H_3N and H_2O; BH_3 and BF_3; BeH_2?

23. The carbon dioxide molecule is diamagnetic and nonpolar; the bond CO is very strong (E = 803 kJ/mole); its internuclear distance d_{CO} is 0.116 nm; it is 0.027 nm shorter than the length of the single CO bond (d_{CO} = 0.143 nm). Explain these experimental data taking into consideration the structure of CO_2 molecule.

24. The BF_3 molecule is triangular and the complex BF_4^- ion has tetrahedral structure. The BF bond in BF_3 (0.129 nm) is shorter than in BF_4^- (0.143 nm). Explain.

25. Explain the difference between structures of the BCl_3, NCl_3 and $BrCl_3$ molecules. Which of them has a dipole moment?

26. A $SnCl_2$ molecule (in the gaseous state) has an angular configuration while a $HgCl_2$ molecule is linear. Explain.

27. What is the spatial configuration of the molecules NOCl, SO_2, $COCl_2$, SO_3, BeF_2, BF_3, NF_3, OF_2? Which of the molecules have dipole moments?

CHAPTER 3

States of Aggregation

3.1. The Gaseous State

1. (a) What is the difference between a real and an ideal gas? Under what conditions can real gases be regarded as ideal ones?

(b) Formulate the laws by Boyle-Mariotte, Charles, Gay-Lussac, Avogadro, Dalton and write the equations of an ideal gas state by Clapeyron and Mendeleev-Clapeyron.

2. Calculate the molecular mass of a gas if its 380 ml weigh 0.5 g at a temperature of 27°C and a pressure of 102.658 kPa.

Experiment 1. Determining the molecular mass of carbon dioxide. Weigh carbon dioxide having a definite volume measured at known temperature and pressure. To that end, stopper tightly a dry flask (approximately, capacity 1 l) and mark the level, to which the stopper enters the neck with a glass writing pencil. Weigh the flask with the air and the stopper to an accuracy of 0.01 g.

Then fill the flask with dry carbon dioxide from a Kipp generator *1* (Fig. 6) or from a cylinder. To dry and purify the gas pass it through scrubbers containing soda solution *2* and solution of concentrated sulphuric acid *3*. Lower a glass outlet tube to the bottom of the flask *4* and pass carbon dioxide. In a while, make sure that all the air is displaced from the flask (use a burning flint). Pull off the outlet tube slowly, then stopper the flask to the mark and weigh. Repeat the procedure several times until the results of weighing show that the flask is filled with carbon dioxide.

Determine the volume of the gas in the flask by filling in water at room temperature to the mark. Measure the temperature and the pressure in the laboratory.

Using the data obtained calculate the masses of air, flask, and carbon dioxide. Calculate the molecular mass of carbon dioxide.

3. Determine the molecular mass of a gas, if its 0.57 g collected above water at a temperature of 27°C and a pressure of 99.962 kPa occupy the volume of 0.5 l.

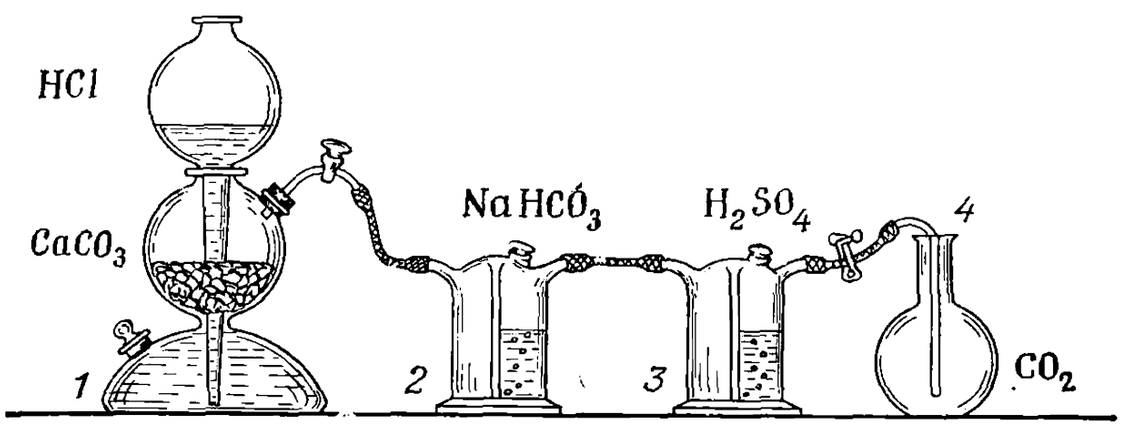


Fig. 6. Obtaining carbon dioxide in a Kipp generator

Experiment 2. Determining the molecular mass of oxygen. The mass and volume of oxygen will be measured at known temperature and pressure.

Obtain oxygen by the thermal decomposition of potassium chlorate (V) using magnesium dioxide as a catalyst. Use the apparatus (Fig. 7) consisting of a test tube *1* containing potassium chlorate (V), two-neck Woulfe bottle (*2*) and a beaker *3*.

Calculate approximately the required quantity of $KClO_3$ bearing in mind that oxygen produced by its decomposition should occupy the volume of 400-500 ml.

Place the calculated amount of potassium chlorate (V) with a small amount of manganese dioxide into the test tube *1*, weigh to an accuracy of 0.01 g and connect it to the apparatus.

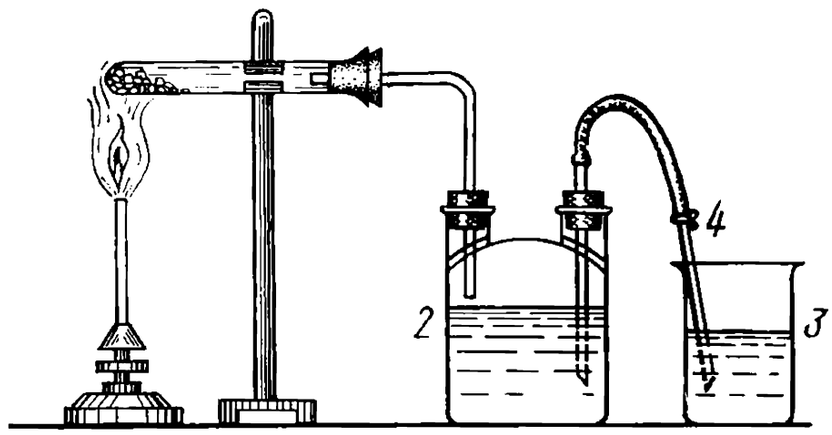


Fig. 7. Apparatus for determining molecular mass of oxygen:
1—a sample of $KClO_3$ in a test tube; *2*—two-neck bottle; *3*—beaker; *4*—clamp

Fill the two-neck Woulfe bottle with tap water at room temperature and close tightly with stoppers through which outlet tubes are passed. Place an accurately measured volume of tap water at room temperature (100-150 ml) in the beaker *3*.

Fill the tube connecting the Woulfe bottle *2* and the beaker *3* with water and test the apparatus for tightness. To that end, move the apparatus to the bench edge and lower the glass end of the tube below the bench level: water should not run from the tube. Otherwise check the connections.

To prevent air entrance into the tube, close it carefully with a clamp *4*. Now lower the tube end into the water in the beaker (*3*) and release the clamp (a hydraulic seal is formed).

Heat the contents of the test tube very carefully. If a white fume forms (KCl sublimes), decrease heating. When 300-400 ml of water pass into the beaker, stop heating. Allow the gas and water in the apparatus to cool to room temperature. Communicate the apparatus with the atmosphere. To that end adjust the position of the beaker (without removing the tube) to equalise the water levels in the beaker and the Woulfe bottle. Wait for a while and close the clamp.

Determine the volume of the obtained oxygen by the volume of the displaced water. Weigh the test tube with the residue. The difference in the masses before and after the experiment is the mass of the oxygen obtained. Note the pressure, temperature of the oxygen and the pressure of water vapour in conditions of the experiment. Use the data obtained to calculate the molecular mass of oxygen.

4. Figure 8 shows the variation of the pV product with p for different real gases and for an ideal gas (pV = const).

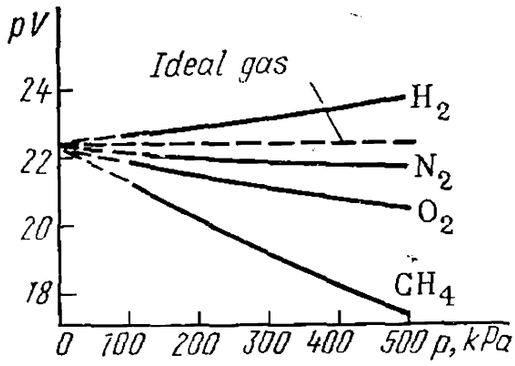


Fig. 8. Variation of pV with p for various real gases at 0 °C

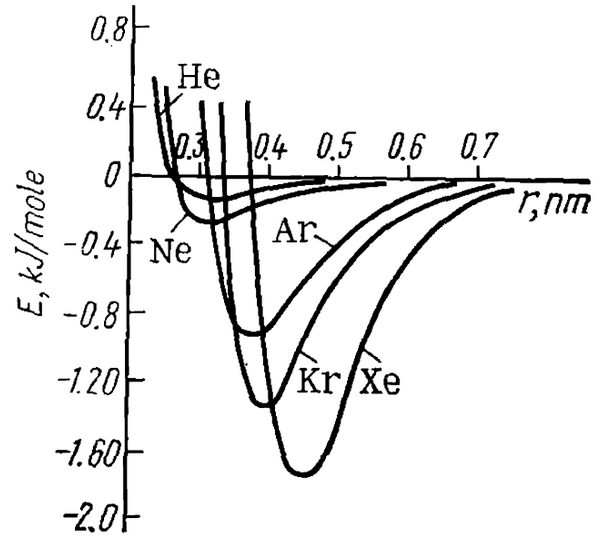


Fig. 9. Energy of intermolecular (interatomic) interaction of inert gases

Explain why real gases do not obey the ideal gas laws (e.g., Boyle-Mariotte law). The deviation from the laws increases with increasing pressure and decreasing temperature of a gas.

5. Figure 9 shows the energy curves of the intermolecular (interatomic) interaction of inert gases. How does the energy of the intermolecular interaction vary in the series He-Ne-Ar-Kr-Xe-Rn? Explain.

6. Draw a diagram of the boiling point variation with the periodic number of the p-element in the series HF (19.5°C)-HCl (—84.9°C)-HBr (—66.7°C)-HI (—35.8°C) and CH_4 (—161°C)-SiH_4 (—112°C)-GeH_4 (—88°C)-SnH_4 (—52°C). Explain the curves.

3.2. The Liquid State

7. (a) An increase in pressure from 1 to 2 kPa decreases a given volume of water by less than 0.04 per cent while an increase in temperature from 0° to 100°C increases the volume only by 2 per cent. The same increase in pressure halves the volume of air and the same increase in temperature increases the volume by 36.6 per cent. Explain.

(b) What is the difference between the structures of the liquid, gas and solid states?

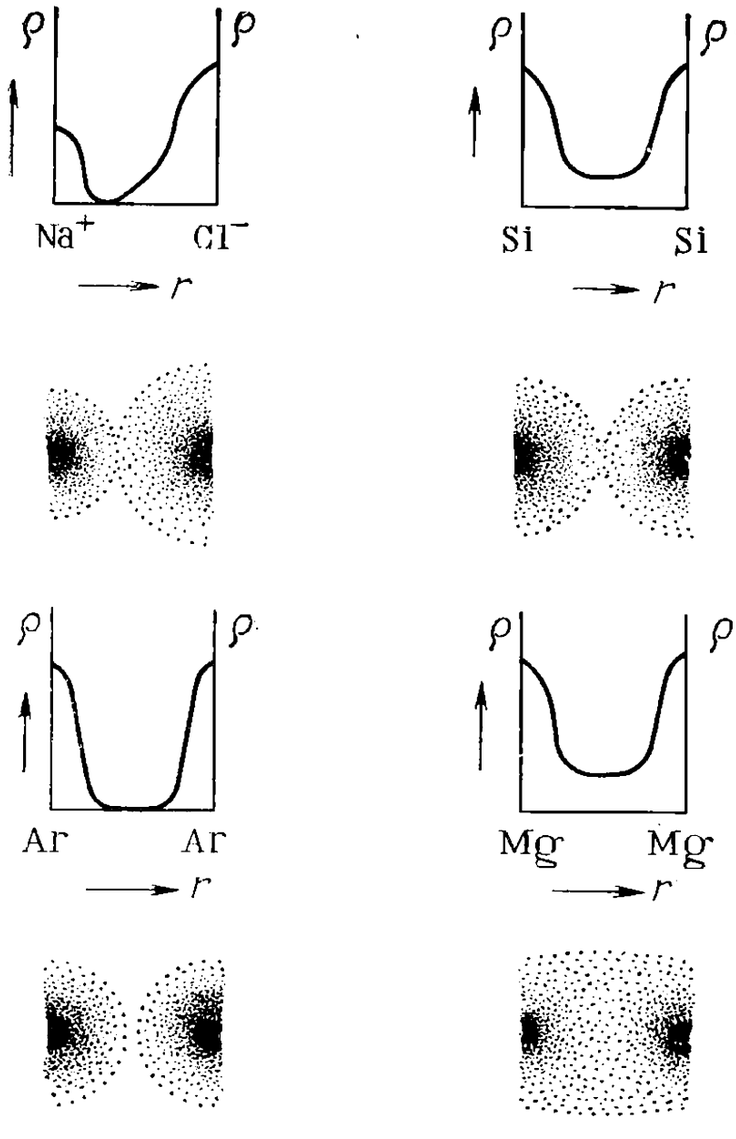


Fig. 10. Electron density distribution (ρ) for various types of chemical bonds depending on the distance between neighbouring atoms

8. Under normal conditions water is liquid and hydrogen sulphide is gas while the molecular mass of water is higher than that of hydrogen sulphide. Why?

9. What is the state of aggregation of amorphous (vitreous) substances?

3.3. The Crystal State

10. Figure 10 shows the variation of the electron density with the distance between neighbouring atoms in selected solid substances.

(a) What type of chemical bond have the crystals of sodium chloride, silicon, magnesium and argon?

(b) What effect has the type of the chemical bond on the melting point and heat of fusion?

	Ar	Si	Mg	NaCl
Melting point, K	83	1683	922	1081
Heat of fusion, kJ/mole . . .	1.17	50.6	8.95	28.5

11. Draw graphs showing the variation of the melting point of inert gases (see Appendix 17) and of the hydrogen compounds of the *p*-elements of the VI group with the number of the period of the *p*-element.

	H_2O	H_2S	H_2Se	H_2Te
Melting point, °C	0	−85.6	−65.7	−51.0

Explain the curves.

12. Determine the stoichiometric composition of A_nB_m compounds formed by the linking of AB_4 unit cells if the bridge bonds A—B—A are formed by (1) one, (2) two, (3) three, and (4) four vertices of each tetrahedron.

13. The melting points of the oxides of the *p*-elements of the 3rd period are:

	Cl_2O_7	SO_3	P_2O_5	SiO_2
Melting point, °C . . .	−93.4	62.2	580	1713

(a) What is the structure of these compounds if their unit cell is a tetrahedron EO_4?

(b) How do their melting points depend on their structure?

14. Determine the stoichiometric composition of A_nB_m compounds whose unit cells are AB_6 octahedra, if the bridge bonds A—B—A are formed by (1) two, (2) four, and (3) six vertices of each octahedron.

15. The melting points of the fluorides of the *p*-elements of the 5th period are:

	TeF_6	SbF_5	SnF_4	InF_3
Melting point, °C . .	−39 (subl)	8	400	1172

(a) What is the structure of these compounds in the solid state if their unit cells is EF_6 octahedron?

(b) Explain the variation of the melting points in the series InF_3-SnF_4-SbF_5-TeF_6.

16. What is the structure type of the following coordination crystals:

(1) MnF_2 and MnO_2, if the coordination number of Mn(II) and Mn(IV) is 6;

(2) BeO and BeF_2, if the coordination number of Be(II) is 4;

(3) MgO and NiO, if the coordination number of Mg(II) and Ni(II) is 6;

(4) Cr_2O_3 and V_2O_3, if the coordination number of Cr(III) and V(III) is 6;

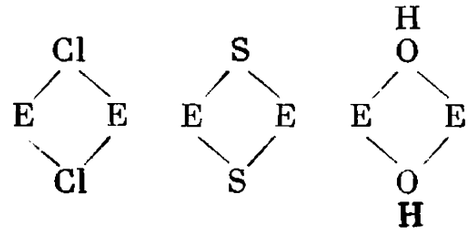
(5) AlF_3, if the coordination number of Al(III) is 6?

17. What is the structure of one layer of laminar crystals of:

(1) $AlCl_3$ and $Al(OH)_3$, if the coordination number of Al(III) is 6;

(2) $MgCl_2$ and $Mg(OH)_2$, if the coordination number of Mg(II) is 6?

18. In fluoro- and oxy-compounds, the neighbouring unit cells are joined by one vertex (on account of bridge bonds E—F—E and E—O—E). In chlorine, sulphide and hydroxy compounds, they are joined by two vertices, bridge bonds



(a) Compare the structure of AlF_3 and $AlCl_3$ and explain the marked difference in their melting points (m.p. of AlF_3 is 1290°C and of $AlCl_3$, 193°C) and solubility.

(b) What is the structure of $BeCl_2$ and SiS_2 if the coordination number of Be(II) and Si(IV) is 4, and the neighbouring tetrahedral unit cells of $BeCl_4$ and SiS_4 are joined by two vertices (edges)?

(c) Compare the structure of $BeCl_2$ and BeF_2, SiS_2 and SiO_2. Explain the marked difference in the melting points of $BeCl_2$ (425°C) and BeF_2 (821°C), SiS_2 (1090°C) and SiO_2 (1713°C).

19. The crystals of LiCl, KCl AgCl have the structure of the NaCl type, the crystals of Si and Ge, of the diamond type, and the crystal of Pb has the Cu structure type. The ionic radii of these substances are as follows:

	Li^+	K^+	Ag^+	Si	Ge	Pb
r, nm . .	0.068	0.133	0.113	0.117	0.122	0.175

(a) Why do the following pairs of substances form substitutional solid solutions (mixed crystals): AgCl and NaCl, Si and Ge?

(b) Why do the following pairs of substances form a eutectic LiCl and NaCl, Ge and Pb?

II

GENERAL PATTERNS AND TYPES OF CHEMICAL REACTIONS

CHAPTER 4

Energy Changes in Chemical and Phase Transformations

1. (a) Why are chemical and phase transformations accompanied by evolution or absorption of energy?

(b) Why is energy evolved in some reactions and absorbed in others?

(c) What changes in a system determine the heat effect of a reaction (phase transformation) proceeding in constant volume and under constant pressure?

2. Formulate the Hess law as applied to the heat effect of the process by which $SbCl_5$ is obtained directly from the simple substances and by a two-step process: formation of $SbCl_3$ from the simple substances and its oxidation with chlorine.

(a) Draw the enthalpy diagram to calculate the heat of formation of antimony pentachloride.

(b) What is the heat of formation (enthalpy)?

3. Using the heats of formation calculate heat effects of the following reactions (at STP):

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$$

$$Fe_2O_3(c) + 2Al(c) = Al_2O_3(c) + 2Fe(c)$$

4. Calculate the heat (enthalpy) of formation of H_2O_2 (l) if the heat of the decomposition

$$H_2O_2(l) = H_2O(l) + 1/2O_2(g)$$

is —98.03 kJ/mole.

5. Calculate the heat of combustion (kJ/cu.m) of a gas mixture of 40 per cent (v/v) of H_2 and 60 per cent (v/v) of CH_4 by heats of combustion of methane and hydrogen.

6. Calculate the heat of formation of HF using the known dissociation energies of F_2, H_2 and HF. Construct the enthalpy diagram to calculate the heat of formation of HF. Compare the calculated value ΔH_f°, for HF with the tabulated data.

7. Calculate the heat of formation of NO by the known dissociation energies of N_2, O_2 and NO. Construct the enthalpy diagram to calculate the heat of formation of NO. Compare the found ΔH_f° for NO with the tabulated data.

Explain why HF is an exothermic compound (see Problem 6) and NO is an endothermic one.

8. Determine the standard heat of formation of the gaseous Cl^- ion if the dissociation energy of the Cl_2 molecule and the electron affinity of the Cl atom are known.

9. Calculate the standard heat of formation of the hydrogen ion H^+ if the energy of dissociation of the hydrogen molecule and the energy of the atom ionization are known.

10. Calculate the heat effect of the interaction of the ions H^+ and Cl^- from heats of formation of HCl(g) and the ions $H^+(g)$ and $Cl^-(g)$.

(a) What is the energy of (1) heterolytic and (2) homolytic decomposition of HCl molecule?

(b) Under what conditions do HCl molecules decompose homolytically and heterolytically?

(c) Can the molecules of HCl fall into ions in water solution if the heats of hydration of the ions $H^+(g)$ and $Cl^-(g)$ are —1108.8 and —351.5 kJ/mole, respectively?

11. Calculate the mean bond energy in CH_4 and SiH_4 molecules, if the heats of formation of H(g), C(g), Si(g) and $CH_4(g)$, $SiH_4(g)$ are known.

Explain the different mean bond energies in CH and SiH.

12. Calculate the mean energy of the H—O bond in the molecule of water, if the heat of formation of $H_2O(g)$, H(g) and O(g) are known.

Construct the enthalpy diagram for the calculation of heat of atomization of water.

13. Using the Born-Haber cycle, calculate the energy of the ionic crystal lattice of potassium chloride, if the enthalpy of formation of KCl (c) and of potassium sublimation, the energies of dissociation of Cl_2 and potassium atom ionization and the electron affinity of the chlorine atom are known. Compare the results of your calculations with those given in the tables.

14. Give the values of heats of hydration and ionic radii of Na^+, Cs^+, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ba^{2+}, F^-, I^-. How does the heat of hydration of an ion depend on its charge and size?

15. Calculate the heat effect of the reactions

$$KOH(sln)+HCl(sln)\rightarrow;\ Cs(OH)(sln)+H_2SO_4(sln)\rightarrow;\ NaOH(sln)+HNO_3(sln)\rightarrow$$

for very dilute solutions with reference to 1 mole of H_2O in standard conditions of pressure and temperature. (a) Why are the heat effects of these reactions the same? (b) Why do heats of neutralization differ for various weak bases and weak acids?

Experiment 1. Determining heat of neutralization of a strong base by a strong acid. A special apparatus called a calorimeter is used for the determination of thermal effects of chemical processes. The reaction is carried out in a calorimetric vessel which is jacketed to prevent the loss of heat and provided with a sensitive thermometer to measure temperature inside the vessel.

An apparatus shown in Fig. 11 can be used for the purpose. It consists of a calorimetric vessel *1* placed inside another vessel *2*. To preclude the loss of heat through the walls, the inner and the outer vessels do not contact each other. This is attained by cork gaskets placed in between the vessels. The calorimetric vessel is provided with a lid *3* with three holes to pass a thermometer *4*, a stirrer 5 and a funnel *6* through which the reactants are introduced into the reaction vessel.

The following formula should be used to calculate the heat Q liberated or absorbed inside the vessel

$$Q = (m_l C_l + m_v C_v)\,\Delta t; \quad \Delta t = t_f - t_i$$

where t_i and t_f are initial and final temperatures in the calorimetric vessel respectively; m_v and m_l are the masses of the calorimetric vessel and the liquid contained in it, respectively; C_v and C_l are specific heats of the glass of the vessel and of the liquid.

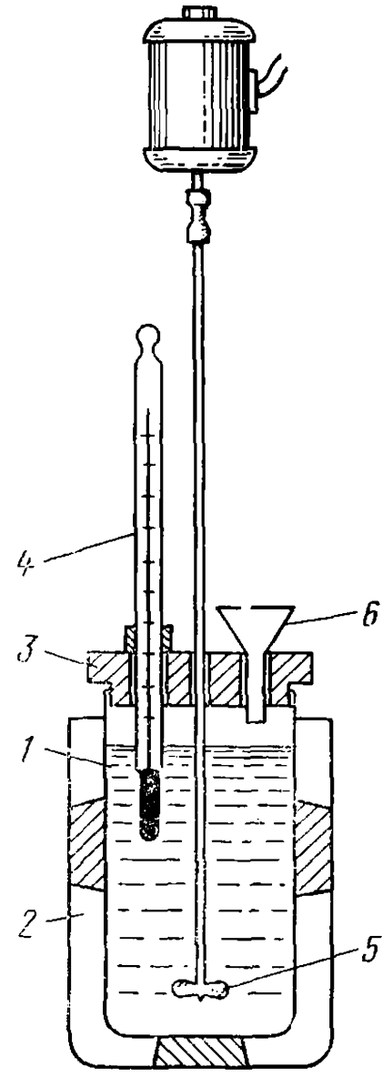


Fig. 11. Calorimeter

Prepare 1.0 N solutions of NaOH (KOH) and HCl (HNO_3), 150 ml of each solution. Weigh the calorimetric vessel. Place the prepared alkali solution into the vessel and measure the temperature to an accuracy of 0.1°C. Measure the temperature of the acid to the same accuracy. Add the acid to the alkali through the funnel (with the stirrer switched on). Record the maximum reading of the thermometer.

Calculate the amount of heat liberated in the reaction. Assume that the initial temperature is the arithmetic mean temperature of the acid and the alkali, while the final temperature is the maximum temperature which is read by the thermometer after adding the acid. The density of the solution is unity, its specific heat is the heat capacity of water, i.e. 4.184 J/g × deg and the specific heat of glass is 0.753 J/g × deg.

Calculate the heat of neutralization of the acid with reference to its equivalent weight. Compare the experimental and the theoretical heats of neutralization. Determine (in per cent) the relative error of the experiment.

Experiment 2. Determining heat of neutralization of a weak base by a weak acid. Carry out the experiment as instructed above, using 1 N solutions of ammonia and acetic acid. Calculate the heat of neutralization with reference to 1 equivalent weight of acetic acid. Compare the results of this and the previous experiment.

16. The dissolution of Na_2SO_4 is accompanied by liberation of heat:

$$Na_2SO_4(c) + aq = Na_2SO_4 \cdot aq, \quad \Delta H^\circ_{298} = -2.9 \text{ kJ/mole}$$

At the same time, the dissolution of the crystal hydrate $Na_2SO_4 \cdot 10H_2O$ is accompanied by absorption of heat:

$$Na_2SO_4 \cdot 10H_2O(c) + aq = Na_2SO_4 \cdot aq, \quad \Delta H^\circ_{298} = 78.7 \text{ kJ/mole}$$

(a) Calculate the heat of hydration of Na_2SO_4.

(b) Explain why the dissolution of some substances is accompanied by liberation and of others by absorption of heat.

(c) How does the solubility of the salts Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ (Fig. 12) depend on temperature? Explain.

17. When 10 g of anhydrous $CaCl_2$ are dissolved in 200 g of water, the temperature of the solution rises by 7.7°C. Calculate the heat of hydration of $CaCl_2$ given the heat of dissolution of $CaCl_2 \cdot 6H_2O$ is 19.08 kJ/mole. Assume the specific heat of the solution to be the same as that of water, i.e. 4.184 J/g × deg.

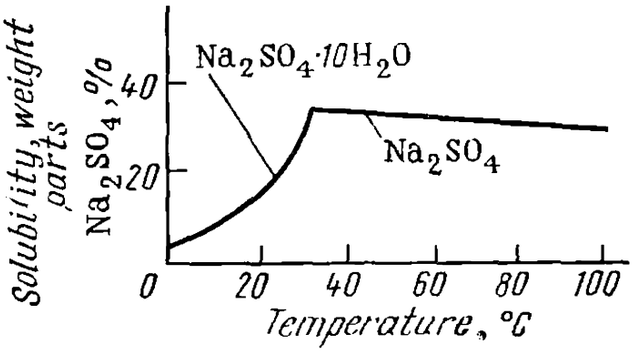


Fig. 12. Variation of solubility in water of Na_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ with temperature

Experiment 3. Determining heat of hydration of cupric sulphate. Carry out the experiment in a calorimeter (see Fig. 11). Weigh the calorimetric vessel, place 300 ml of distilled water into it and measure the temperature of water to an accuracy of 0.1°C.

Weigh out about 8 g of cupric sulphate to an accuracy of 0.01 g and add it quickly and carefully to the water in the calorimetric vessel. Stir carefully and watch the temperature changes. Record the maximum reading of the thermometer.

Calculate the amount of heat liberated during the dissolution of $CuSO_4$. Assume the temperature of water as the initial temperature and the maximum temperature of the solution as the final temperature. Let the density of the solution be unity, its specific heat be that of water (4.184 J/g × deg) and the specific heat of glass be 0.753 J/g × deg. Calculate the heat of dissolution of 1 mole of $CuSO_4$.

Repeat the experiment and calculations for the crystal hydrate $CuSO_4 \cdot 5H_2O$ (a sample about 10 g).

Use the found heats of dissolution of cupric sulphate $CuSO_4$ and $CuSO_4 \cdot 5H_2O$ to calculate the heat of hydration of cupric sulphate.

Experiment 4. Determining heat of hydration of sodium carbonate. Carry out the experiment as instructed above. The weight of the

sample of anhydrous sodium carbonate should be about 7 g and that of the crystal hydrate, about 15 g. The amount of water should be 300 ml.

CHAPTER 5

The Enthalpy and Entropy Factors and the Direction of a Process

1. What is entropy? Explain the shape of the curve shown in Fig. 13.

2. Calculate ΔS°_{298} of the following reactions:

(1) $Al(c) + Sb(c) = AlSb(c)$
(2) $C(graphite) + CO_2(g) = 2CO(g)$
(3) $C(graphite) + O_2(g) = CO_2(g)$
(4) $3H_2(g) + N_2(g) = 2H_3N(g)$
(5) $NH_4NO_3(c) = N_2(g) + 2H_2O(g) + 1/2O_2(g)$

In these reactions $\Delta S > 0$, $\Delta S < 0$ or $\Delta S \approx 0$. Why?

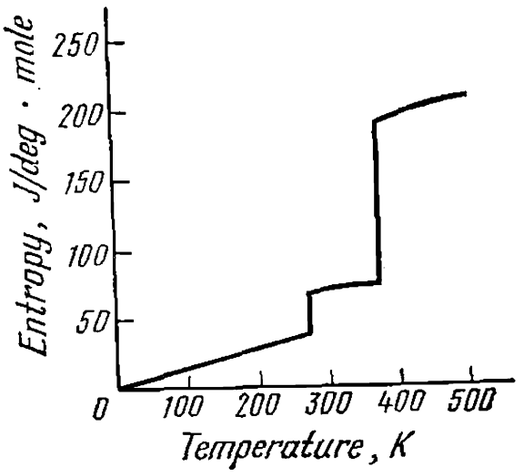


Fig. 13. Variation of entropy of water with temperature

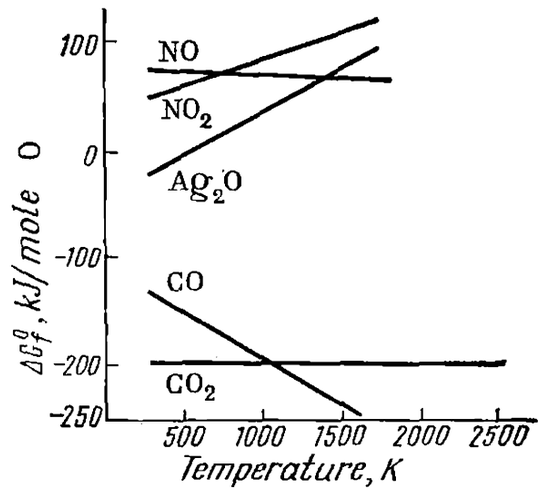


Fig. 14. Variation of ΔG°_f with temperature

3. What is the Gibbs free energy? Define conditions under which a given process is realizable or impossible or is at the state of equilibrium.

4. Calculate variation of the enthalpy, entropy and the Gibbs free energy for oxidation of NO to NO_2 under standard conditions.

(a) Will the reaction occur at 25°C?

(b) What factor (enthalpy or entropy) determines the sign of the ΔG°_{298} in this reaction?

5. Calculate variation of the Gibbs free energy at 25 and 1000°C for the following reaction:

$$C(graphite) + H_2O(g) = H_2(g) + CO(g),$$
$$\Delta H^\circ_{298} = 131.3 \text{ kJ/mole}, \quad \Delta S^\circ_{298} = 133.7 \text{ J/deg·mole}$$

(Disregard the effect of temperature on ΔH and ΔS).

(a) Under what specified temperature conditions will the reaction occur in principle?

(b) What factor (enthalpy or entropy) determines the possibility of this reaction?

6. Figure 14 shows variation of the ΔG_f° of some reactions with temperature.

(a) In what reactions does the entropy of the system increase ($\Delta S > 0$) and what effect it has on the shape of the curves $\Delta G_f^\circ = f(T)$?

(b) In what reactions does the entropy of the system decrease ($\Delta S < 0$) and what effect it has on the shape of the curves showing the variation of ΔG with temperature?

(c) Which of the reactions mentioned are promoted and which are inhibited by the rising temperature?

(d) Why is the value of ΔG_f° of the reaction

$$C(\text{graphite}) + O_2(g) = CO_2(g)$$

practically not affected by temperature changes (see Problem 2)?

7. Using Fig. 14, explain the following:

(a) What temperature conditions are required for the synthesis of NO from the simple substances?

(b) Can NO_2 be synthesized directly from the simple substances?

(c) At what temperature conditions is Ag_2O formed from the simple substances and at what temperature is it decomposed?

8. Calculate ΔH°_{298}, ΔS°_{298} and ΔG°_{298}

$$NH_4Cl(c) = H_3N(g) + HCl(g)$$

How does the direction of the given process depend on temperature?

Experiment 3. Formation and thermal decomposition of ammonium chloride. Place a pinch of NH_4Cl into a test tube provided with an outlet tube. Heat the test tube carefully. Observe the disappearance of NH_4Cl from the bottom and appearance of a white deposit on cold walls of the test tube and of the outlet tube. Explain.

9. Calculate ΔG°_{298} of the following reactions:

(1) $MgO(c) + CO_2(g) = MgCO_3(c)$

(2) $BaO(c) + CO_2(g) = BaCO_3(c)$

(3) $CaO(c) + CO_2(g) = CaCO_3(c)$

(4) $SrO(c) + CO_2(g) = SrCO_3(c)$

How do the acid-base properties change in the series of the oxides MgO-CaO-SrO-BaO and how do these changes agree with ΔG of formation of said carbonates from the oxides?

CHAPTER 6

Chemical Equilibrium

6.1. General Concepts

1. Write the expression for equilibrium constants of the following reactions:

$$CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$$
$$2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)$$
$$CO(g) + H_2O(\text{vapour}) \rightleftarrows CO_2(g) + H_2(g)$$
$$H_3N(sln) + H_2O(l) \rightleftarrows NH_4^+(sln) + OH^-(sln)$$
$$CH_3COOH(sln) \rightleftarrows CH_3COO^-(sln) + H^+(sln)$$
$$H_2O(l) \rightleftarrows H^+(sln) + OH^-(sln)$$
$$[HgI_4]^{2-}(sln) \rightleftarrows Hg^{2+}(sln) + 4I^-(sln)$$
$$MgCO_3(c) \rightleftarrows MgO(c) + CO_2(g)$$
$$3Fe(c) + 4H_2O(g) \rightleftarrows Fe_3O_4(c) + 4H_2(g)$$

Explain the different expression of the equilibrium constants for homogeneous and heterogeneous system?

2. Determine ΔG°_{298} and the equilibrium constant K_{eq} at 298 K for

$$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$$

3. Formulate the Le Chatelier principle. Explain the experimental data on the ammonia synthesis given in Fig. 15.

4. A reversible reaction

$$2NO_2(g) \rightleftarrows N_2O_4(g), \quad \Delta H < 0$$

occurs in a mixture of NO_2 (brown) and of N_2O_4 (colourless).

(a) What is the temperature effect on the equilibrium of the system? What effect will it have on the colour of the mixture?

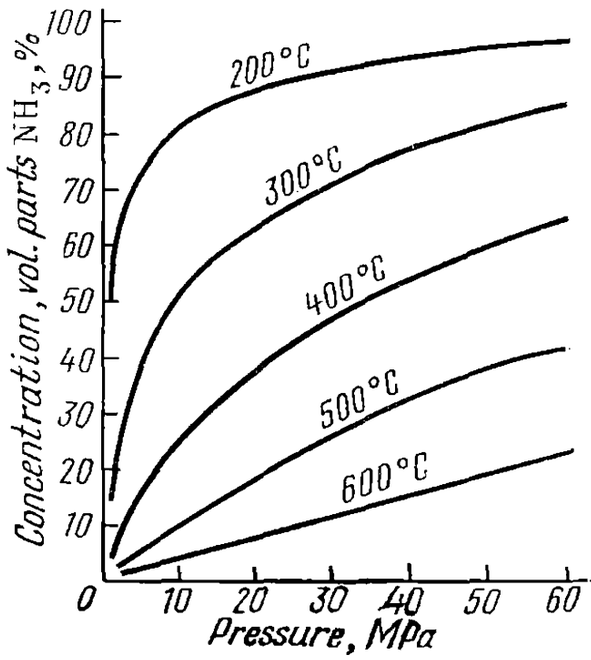


Fig. 15. Equilibrium concentrations of ammonia in nitrogen-hydrogen mixture ($N_2 + 3H_2$) depending on temperature and pressure

Experiment 1. Effect of temperature on equilibrium. Use the apparatus shown in Fig. 16. Fill it with a mixture of NO_2 and N_2O_4 and place one ball into a beaker filled with hot water, and the other into a beaker containing cold water or ice. Explain your observations.

5. Write the expression of the equilibrium constant for the reversible reaction:

$$FeCl_3(sln) + 3KCNS(sln) \rightleftarrows Fe(CNS)_3(sln) + 3KCl(sln)$$

In what direction will the equilibrium be shifted by the addition of KCNS; $FeCl_3$; KCl? How will it affect the colour of the system? Own colour of $Fe(CNS)_3$ is intense red.

Experiment 2. Effect of reactant concentration on equilibrium. Mix 10-ml portions of dilute solutions of $FeCl_3$ and NH_4CNS in a beaker. Divide the obtained solution between four test tubes. Keep one for reference. Add 2-3 drops of concentrated solutions of $FeCl_3$ and NH_4CNS into the second and the third test tubes respectively. Add NH_4Cl crystals into the fourth test tube. Explain your observations.

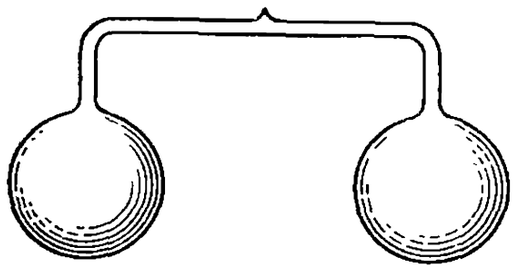


Fig. 16. Apparatus filled with $NO_2 \rightleftarrows N_2O_4$ mixture

6. Calculate ΔH°_{298}, ΔS°_{298} and the temperature of decomposition of crystalline (1) $CaCO_3$; (2) $MgCO_3$; (3) $BaCO_3$ at which CO_2 pressure is 0.1 MPa. Mind that ΔH and ΔS do not depend on temperature.

Arrange the carbonates in the order of their increasing thermal stability. Compare the obtained series with the data given in Problem 9 (Ch. 5).

Experiment 3. Comparing thermal stability of carbonates. Place powdered $CaCO_3$ and $BaCO_3$ into two separate test tubes provided with outlet tubes. Lower the outlet tubes into a beaker containing $Ca(OH)_2$ solution. Heat the test tubes. In which of them will CO_2 evolve earlier? Explain.

6.2. Homogeneous Equilibrium in Electrolyte Solutions

7. Figure 17 shows the curves of potential energy of an ion removal from the crystal lattice in vacuum and in solvent.

(a) Why does the removal of an ion from the crystal lattice in vacuum require higher energy than in solvent?

(b) In what medium is it easier to separate two oppositely charged ions, in water (the dielectric constant is 80) or in ethyl alcohol (the dielectric constant is 25.4)?

8. Explain the different solubility of electrolytes in water and ethanol and the different conductivity of the solutions obtained. (The solubilities below are given in grams per 100 g of the solvent.)

	NaCl	KCl	NaBr	KBr
In water	35.9	33.0	88.8	65.9
In ethanol	0.07	0.003	2.3	0.14

Experiment 4. Comparing solubility of salt in water and ethanol. Place water and ethanol into two separate test tubes. Add a pinch of sodium chloride into each of them. Explain your observations.

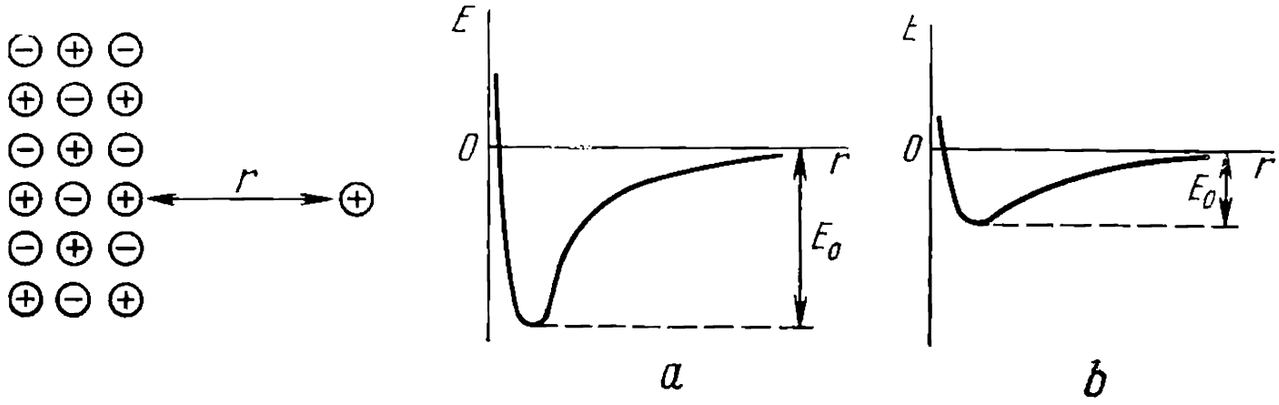


Fig. 17. Potential energy curves of ion removal from crystal lattice in vacuum (*a*) and in dielectric (*b*)

Experiment 5. Conductivity of solutions. Use an apparatus shown in Fig. 18. Compare conductivities of 0.1 *N* aqueous and alcoholic solutions of potassium nitrate and potassium hydroxide. To that end, place 50 ml of solution under study into a 100-ml beaker, and lower carbon electrodes into the liquid. (Rinse the electrodes in distilled water before the experiment.) Switch on the current and read the ammeter. Lower the electrodes to the same depth. Explain the different conductivity of aqueous and alcoholic solutions of one and the same substance.

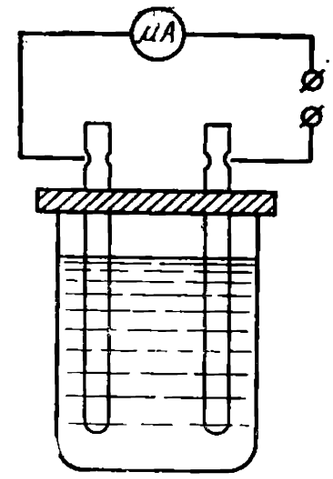


Fig. 18. Measuring electrical conductivity of solutions

9. (a) Define the activity of the ion (*a*); how does it depend on the analytical (overall) concentration (*C*) of the ion?

(b) In what case is the activity coefficient close to unity and the ion concentration can thus be used instead of it in calculations?

10. The strength of oxyacids depends on the number of peripheral oxygen atoms (not bound in the OH radical):

	$(HO)_nE$	$(HO)_nEO$	$(HO)_nEO_2$	$(HO)_nEO_3$
K_1	10^{-8}-10^{-11}	10^{-2}-10^{-4}	high	very high
pK_1	8-11	2-4	-1-(-3)	-10
Acid strength	weak	moderate	strong	very strong

(a) Explain this regularity.

(b) Classify the following acids by their strength: HNO_3, HClO, H_2SO_3, H_6TeO_6, H_2SO_4. To prove your answer give the ionization constants of the acids.

(c) How does the acid strength vary in the series $HClO$-$HClO_2$-$HClO_3$-$HClO_4$; H_4SiO_4-H_3PO_4-H_2SO_4-$HClO_4$? Explain. Compare the ionization constants of the acids.

Experiment 6. Conductivity of acid solutions. Place 0.1 *N* solutions of acids of different strength into three dry beakers and try them for conductivity using the apparatus shown in Fig. 18. Record the instrument readings. Arrange the acids in the order of their increasing activity.

Experiment 7. Action of equinormal acids on metals. Pour 10-ml portions of 0.1 *N* solutions of hydrochloric, sulphuric and acetic acids into three test tubes. Drop three pieces of magnesium of the same length and width (weighing maximum 0.2 g) into the test tubes. Note in which acid magnesium dissolves faster. Explain why.

Experiment 8. Conductivity of aqueous solutions of ammonia and metal hydroxides. Test 1 *N* solutions of hydroxides of sodium and potassium and ammonia solution for conductivity. Explain your observations.

11. Write expressions of the ionization constants of orthophosphoric acid. Give the values of K_1, K_2 and K_3.

(a) How do they relate? Explain.

(b) The presence of what ions is most probable in the solution of orthophosphoric acid?

12. Write the equations of ionization and the ionization constants for acetic acid and ammonia in water.

(a) How does the addition of sodium acetate to acetic acid solution and of an ammonium salt to ammonia solution affect the equilibrium state?

(b) How do the ions of the same charge affect the dissociation of a weak electrolyte?

Experiment 9. Effect of ions of the same charge on dissociation of weak electrolyte. Add methyl orange to two test tubes containing 0.1 *M* acetic acid. Keep one of them as control and place sodium acetate in the other. Compare the colour of the indicator in this test tube with that in the control test tube.

In the same way, test a 0.1 *M* ammonia solution using phenolphthalein as an indicator. Add ammonium chloride to the ammonia solution. Explain your observations.

13. What is the concentration of H^+ ions and the pH of the medium if the concentration of the OH^- ions is: (1) 10^{-8} mole/l; (2) 10^{-2} mole/l?

14. Calculate the concentration (mole/l) of the H^+ and the OH^- ions in a solution whose pH is 4.3.

15. Calculate the pH of the following solutions assuming them to be fully dissociated: (1) 0.01 *M* HCl; (2) 0.005 *M* HCl; (3) 0.01 *M* KOH; (4) 0.05 *M* KOH.

16. Below are given pH ranges for the colour change of some acid-base indicators:

Indicator	Colour change	pH range
Methyl yellow	red — yellow	2.9-4.0
Methyl orange	red — yellow	3.1-4.4
Methyl red	red — yellow	4.4-6.3
Litmus	red — blue	5.0-8.0
Phenolphthalein	colourless — red	8.0-9.8
Alizarine yellow	yellow — lilac	10.0-12.0

(a) What is the reaction of the medium (acid, neutral or alkaline) in which the colour of methyl orange, methyl red, litmus and phenolphthalein is changed?

(b) Can methyl orange be used to identify (1) a moderately acid medium (pH about 3) from a weak acid medium (pH about 5.6); (2) a weak acid medium from a neutral medium; (3) a neutral medium from an alkaine medium?

(c) Can phenolphthalein be used to differentiate between (1) an acid and a neutral medium; (2) a neutral and a weak alkaline medium (pH 8); (3) a weak alkaline from a moderately alkaline medium (pH 11)?

Experiment 10. The colour of indicator and pH. Examine the operating instructions for pH-meter. (a) Using a pH-meter, determine the pH of neutral, acid and alkali solutions. To that end, place distilled water, 0.1 *M* hydrochloric acid solution and 0.1 *M* alkali solution into three beakers and measure the pH of the liquids.

(b) Divide the contents of each beaker between three test tubes. Determine the colour of indicators in each solution. To that end, add one drop of litmus, methyl orange and phenolphthalein into each test tube. Write down the results into the following table:

Indicator	pH range*	Medium		
		Neutral	Acid	Alkaline
Litmus } pH colour				
Methyl orange } pH colour				
Phenol-phthalein } pH colour				

* See Problem 16.

Experiment 11. Tentative determination of pH by universal test paper. Universal indicators are used for tentative determination of pH solutions. The universal indicator is a mixture of several

indicators which change their colour at different pH. Universal test paper is used for the same purpose as well. A colour change chart, which is supplied together with the test paper, is used for the determination of pH of solutions by colour matching.

Using a glass rod, apply 2 or 3 drops of a test solution onto a sheet of universal test paper. Compare the colour of the wet spot with the colour matching chart. Determine tentatively the pH of the test solution.

6.3. Heterogeneous Equilibrium in Electrolyte Solutions

17. Calculate the solubility of salts (mole/l) if their content in a saturated at 20°C solution is: (1) 8 g/l of Ag_2SO_4; (2) 0.43 g/l of $MgCO_3$; (3) 0.11 g/l of $SrSO_4$.

18. Calculate the solubility of $BaSO_4$ in (a) mole/l; (b) g/l from the solubility product of $BaSO_4$.

19. (a) Using the solubility product values, calculate the solubility at 25°C of silver halides (AgCl, AgBr and AgI) and the concentration of each ion in mole/l and g/l.

(b) How does the solubility change in the series AgCl-AgBr-AgI?

(c) Which ion, Cl^-, Br^- or I^-, is the most sensitive reagent for identification of Ag^+ in solution?

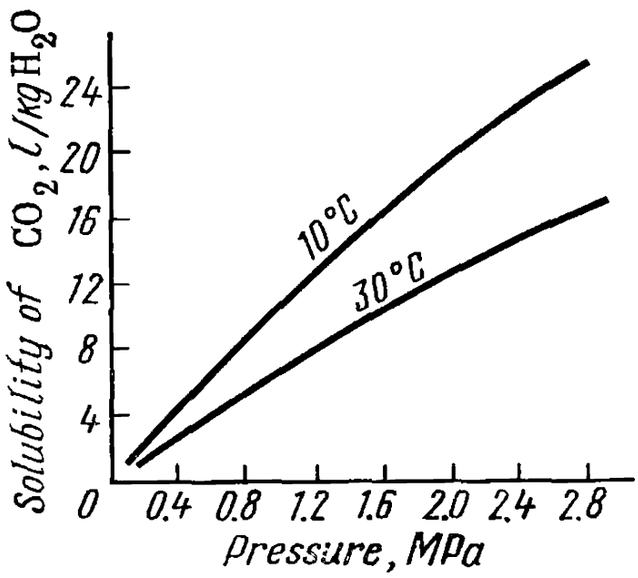


Fig. 19. Solubility of CO_2 in water (volume of CO_2 is reduced to normal conditions)

20. (a) How does the solubility product change in the series of carbonates of Be(II)-Mg(II)-Ca(II)-Sr(II)-Ba(II)?

(b) Calculate the solubility of the salts (mole/l).

Experiment 12. Constructing the solubility curve by experimental data.

The concentration of a saturated at a given temperature solution of a substance can be determined as follows. Weigh a porcelain dish. Prepare a saturated solution of a given substance. To that end, grind the substance to powder and add it by small portions to distilled water in a warmed beaker. Heat the solution to the required temperature and add the powder until it stops dissolving. Stir the solution continually with a glass rod. Keep the saturated solution for a few minutes at the given temperature. Transfer quickly 20 ml of the solution into a weighed porcelain dish and weigh the sample. Evaporate the solution, cool the dish in a desiccator and weigh the dry residue. Calculate the concentration of the saturated test solution.

Use your own data and the data of your mates (obtained for other temperatures) to construct the solubility curve.

Experiment 13. Comparing temperature effect on solubility of salts. Place 50-ml portions of water in three beakers and measure the temperature. Add 0.1 mole of the following salts: ammonium nitrate, anhydrous sodium sulphate and sodium sulphate decahydrate. Measure the temperature in each beaker and follow up its changes. Explain your observations.

Construct the solubility curves for given salts using the table given in Appendix 21. What dependence can be found between the sign of the heat of solution of the given substance and the variation of its solubility with changing temperature?

21. Figure 19 shows the effect of temperature and pressure on the solubility of carbon dioxide in water. Explain the given data.

CHAPTER 7

Reactions Without Alteration of the Oxidation State of Elements

7.1. Exchange Reactions

1. Calculate the variation of the Gibbs free energy (at STP) for the following reactions:

$BaCl_2(sln) + Na_2SO_4(sln) \rightarrow$	$HgS(c) + HCl(sln) \rightarrow$
$Na_2CO_3(sln) + HCl(sln) \rightarrow$	$NaCl(c) + CH_3COOH(sln) \rightarrow$
$KOH(sln) + H_2SO_4(sln) \rightarrow$	$NaClO(c) + CH_3COOH(sln) \rightarrow$
$NaCl(sln) + KNO_3(sln) \rightarrow$	$ZnSO_4(sln) + NaOH(sln) \rightarrow$
$ZnS(c) + HCl(sln) \rightarrow$	$NaCl(sln) + KOH(sln) \rightarrow$

(a) Which of the reactions are realizable? Explain your answer.

(b) Formulate the conditions for practically irreversible and complete ionic reactions.

(c) Formulate the conditions for the formation of acids and alkalis from salts in exchange reactions.

(d) By what reactions are carbon dioxide and hydrogen sulphide obtained in the Kipp generator and why do the reactions proceed practically to the end?

Experiment 1. Ionic reactions proceeding practically irreversibly and to the end. (a) Add hydrochloric acid, by drops, to sodium silicate solution. Explain your observations.

(b) Add concentrated sulphuric acid to the test tube containing solid sodium chloride (use the hood!) and heat. Examine the evolving gas by a moist blue litmus paper. Explain your observations.

(c) Substantiate the selection of reaction partners and obtain the hydroxide of the corresponding metal by an exchange reaction.

(d) Obtain $PbSO_3$ and PbS by an exchange reaction between the appropriate solutions. Separate the precipitates on a centrifuge and examine their attitude to hydrochloric acid. Explain your observations.

2. (a) How do the solubility product and the strength of alkali change in the series Mg(II)-Be(II)-Ca(II)-Sr(II)-Ba(II)?

(b) Why is $Be(OH)_2$ precipitated from solutions at lower pH (8.81) than $Mg(OH)_2$ (12.4)?

3. How does the solubility product of sulphates change in the series Ca(II)-Mg(II)-Ba(II)? Predict the solubility of $BeSO_4$ and $MgSO_4$ in water.

Experiment 2. Comparing solubility of sulphates of the *s*-elements of group II. Add equal number of drops of sodium sulphate solution to equal volumes of equimolar solutions of chlorides of magnesium, calcium and barium contained in separate test-tubes. Compare the amounts of precipitates in the test-tubes and explain.

4. Calculate equilibrium concentration of ions in saturated solutions of $PbSO_4$ and PbS from their solubility products. What ion, SO_4^{2-} or S^{2-}, is more sensitive for the analytical determination of the Pb^{2+} ion?

Experiment 3. Comparing solubility of sparingly soluble compounds. Add sodium sulphate solution to a test tube containing lead(II) nitrate. Separate the precipitate on a centrifuge. Add ammonium sulphide solution to the filtrate. Stir the mixture. Explain your observations.

Experiment 4. Formation of mixed crystals. Precipitate $BaSO_4$ and AgCl from barium and silver salt solutions containing $KMnO_4$. What precipitate is coloured? Explain.

5. Calculate ΔG°_{298} of the reactions with reference to 1 mole of H_2O:

$$KOH(sln) + HNO_3(sln) \rightarrow; \quad RbOH(sln) + H_2SO_4(sln) \rightarrow;$$
$$NaOH(sln) + HCl(sln) \rightarrow$$

Why are the values of ΔG°_{298} equal?

6. Calculate ΔG°_{298} of the reactions with reference to 1 mole of H_2O:

$$Mg(OH)_2(c) + HCl(sln) \rightarrow; \quad Mg(OH)_2(c) + H_2SO_4(sln) \rightarrow$$

Why are the values of ΔG°_{298} different from those calculated in Problem 5?

7. To neutralize 20 ml of sulphuric acid, 25 ml of 0.005 *M* sodium hydroxide solution were spent. Determine the normality of sulphuric acid.

8. What volume of a 0.1 *M* sodium hydroxide solution is necessary to neutralize 10 ml of 10 per cent nitric acid (density, 1.056 g/cc)?

7.2. Hydrolysis

9. Use heats of hydration of the cations Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Al^{3+}, Fe^{3+}, Fe^{2+} to characterize their donor-acceptor properties in the reaction with water molecules and the variation of these properties with the charge and the size of the cation.

10. The constants of hydrolysis with reference to the cation (acid ionization of aquo complexes) at 25°C are given below:

	Na^+	Mg^{2+}	Ca^{2+}	Ba^{2+}	Al^{3+}	Fe^{2+}	Fe^{3+}
pK_{hydr} . . .	15	11.4	12.6	13.2	5.1	9.5	2.2

(a) Write the expression for the hydrolysis constant with the participation of the ions Fe^{2+} and Fe^{3+}.

(b) What dependence exists between the charge and the size of the cation and its susceptibility to hydrolysis?

(c) What relationship exists between the susceptibility of the cation to hydrolysis and the ability of its hydroxide to basic ionization (base strength)?

11. The energy of the hydrogen bond between the anion EO_4^{n-} and water molecules increases in the series ClO_4^--SO_4^{2-}-PO_4^{3-}-SiO_4^{4-} from 7.1 to 35.6 kJ/mole.

(a) Write the expression of the hydrolysis constant for the anion ClO_4^- and PO_4^{3-}.

(b) What dependence exists between the charge and the size of the anion and its susceptibility to hydrolysis?

(c) What relationship exists between the anion susceptibility to hydrolysis and the ability of the acid formed to acid ionization (acid strength)?

(d) How does the susceptibility to hydrolysis change in the series ClO_4^--SO_4^{2-}-PO_4^{3-}-SiO_4^{4-}?

Experiment 5. Determining pH of solutions. (Hydrolysis by cation). Determine the pH of 1 *N* solutions of aluminium sulphate and sodium sulphate using a pH-meter. Investigate the reaction of the medium using indicator. Compare the results.

Write the equations of hydrolysis. Enter the results of this and next experiments into the table below:

Nos	Compound	pH	Medium	Indicator colour	Reaction equations

12. Figure 20 shows the effect of the cation nature on the pH of the solution of oxychlorates(VII) of *s*- and *d*-elements of group II, $M(ClO_4)_2$.

(a) How does the hydrolysis by cation change in the series Be^{2+}-Mg^{2+}-Ca^{2+}-Sr^{2+}-Ba^{2+} and how can it be explained?

(b) Compare the attitude to hydrolysis of $Ca(NO_3)_2$ and $Zn(NO_3)_2$, given pK_{hydr} ($pK_{hydr} = -\log K_{hydr}$) for the ions Ca^{2+} and Zn^{2+} is 12.6 and 8.8 respectively. Write the equation for hydrolysis.

Experiment 6. Attitude of $MgCl_2$ and $BaCl_2$ to hydrolysis. Use a pH-meter to determine the pH of 1 *N* solutions of $MgCl_2$ and $BaCl_2$. Explain your observations.

Experiment 7. Comparing the character of hydrolysis by cation of salts of *s*- and *d*-elements of group II. Dissolve crystalline $Ca(NO_3)_2$ and $Zn(NO_3)_2$ in distilled water and determine the reaction of the medium. Give your explanations.

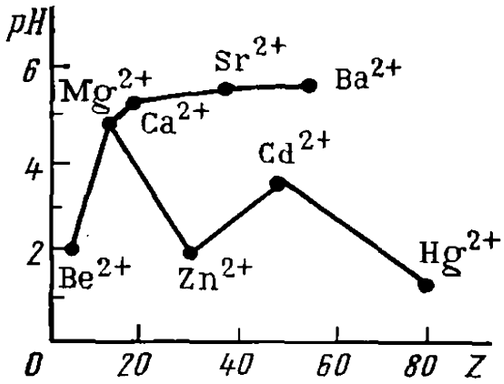


Fig. 20. Variation of pH of aqueous solution of $M(ClO_4)_2$ with the atomic number of elements in group II

Experiment 8. Determining pH of solutions. (Hydrolysis by anion). Determine the pH of 1 *N* solutions of sodium sulphate and sodium phosphate using a pH-meter. Investigate the reaction of the medium by indicator. Explain the results obtained and enter them into the table.

13. Give expressions of constants for three ionization steps of H_3PO_4 and of constants of stepped hydrolysis by the anion PO_4^{3-}.

Which step of hydrolysis by the anion PO_4^{3-} is deeper and why?

Experiment 9. Comparing hydrolysis of Na_3PO_4, Na_2HPO_4 and NaH_2PO_4. Determine the pH of 1 *N* solutions of NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 by a pH-meter and indicator. Explain your observations.

14. Write expressions for the constants of hydrolysis of Na_2CO_3 and $CuCl_2$.

(a) In what direction will the equilibrium of these reactions displace if acid is added to one solution and alkali to the other?

(b) When some salts (for example $Pb(NO_3)_2$ or $SnCl_2$) are dissolved in water, the solution is acidified. Why?

(c) How does the degree of hydrolysis depend on dilution?

Experiment 10. Shifts in equilibrium of hydrolysis. Effect of ions of the same charge and dilution of solution. (a) Dissolve crystalline $Pb(NO_3)_2$ in water: the solution becomes cloudy. Add a few drops of HNO_3. Explain your observations.

(b) Place concentrated solution of $SbCl_3$ into a test tube and add, dropwise, water until precipitation starts. Add, also by drops, hydrochloric acid. Explain your observations, assuming that the hydrolysis proceeds as follows

$$SbCl_3(sln) + H_2O(l) \rightleftarrows SbOCl(s) + 2HCl(sln)$$

(c) Determine the pH of a 0.5 *N* solution of $Bi(NO_3)_3$ or $SbCl_3$. Add an equal volume of water and measure the pH again. Explain

the results of the experiment. The hydrolysis of $Bi(NO_3)_3$ proceeds as follows:

$$Bi(NO_3)_3 + H_2O \rightleftharpoons BiONO_3 + 2HNO_3$$

15. What effect does temperature produce on the equilibrium

$$H_2O \rightleftharpoons H^+ + OH^-$$

and what effect has it on the degree of hydrolysis of a compound when the solution is heated?

Experiment 11. Effect of heat on hydrolysis of sodium acetate. Place sodium acetate solution into a flask and add 1-2 drops of phenolphthalein. Heat to the boil. Explain the different colour of the solution in the hot and cooled state.

Experiment 12. Dissolving zinc in the product of hydrolysis of zinc(II) chloride. Drop a granule of zinc into a solution of zinc(II) chloride and heat. Explain the evolution of hydrogen.

16. Give the equation of hydrolysis by cation Fe^{3+} assuming that the following are formed: (1) uninuclear complexes $FeOH^{2+}$ and $Fe(OH)_2^+$; (2) dinuclear complexes $Fe_2(OH)_2^{4+}$, and (3) multinuclear hydroxy- and oxy-complexes. In what conditions of hydrolysis are these products formed?

Experiment 13. Effect of heat on hydrolysis of $FeCl_3$ and $AlCl_3$. (a) Place a few drops of concentrated solution of $FeCl_3$ into test tubes containing cold and hot water. Explain the different colour of the resultant solutions.

(b) Measure the pH of a 0.5 *N* solution of $AlCl_3$ ($FeCl_3$). Heat the solution to 60°C and measure the pH again. Compare the results of measurements and explain.

17. Calculate ΔG°_{298} for the reactions:

(1) $2Al^{3+}(sln) + 3S^{2-}(sln) = Al_2S_3(c)$

(2) $2Al^{3+}(sln) + 6H_2O(l) + 3S^{2-}(sln) = 2Al(OH)_3(c) + 3H_2S(sln)$

(a) What process is more probable thermodynamically?

(b) What is the mechanism of mutual intensification of hydrolysis of salts? Can Al_2S_3 be precipitated in an exchange reaction in an aqueous solution?

(c) What products are formed if solutions of $AlCl_3$ and Na_2CO_3 are mixed?

Experiment 14. Reaction of solutions of compounds mutually intensifying the hydrolysis of one another. Add, by drops, a solution of sodium carbonate to a solution of aluminium chloride or aluminium sulphate until precipitation begins. Carry out the same experiment with solutions of chromic chloride, or chromic sulphate, and ammonium sulphide.

Prove experimentally that the reaction between these solutions gives aluminium hydroxide and chromic hydroxide respectively.

18. What mechanism can explain hydrolysis of $SnCl_4(TiCl_4)$ giving hydrated oxide $SnO_2 \cdot nH_2O$ $(TiO_2 \cdot nH_2O)$?

Experiment 15. Hydrolysis of $SnCl_4$. Explain the appearance of white fumes when a bottle containing $SnCl_4$ is opened.

19. Which of the reactions of hydrolysis given below is reversible and which is irreversible in normal conditions?

$$PCl_3(l) + 3H_2O(l) = H_3PO_3(sln) + 3HCl(sln)$$
$$AsCl_3(l) + 3H_2O(l) = H_3AsO_3(sln) + 3HCl(sln)$$

Calculate ΔG°_{298}.

Experiment 16. Hydrolysis of phosphorus trichloride. Open the bottle containing PCl_3. Explain the white fumes.

CHAPTER 8

Reactions with Alteration of the Oxidation State of Elements

8.1. Making out Equations of Oxidation-Reduction Reactions

1. Using the electron-balance method, complete the following equations of oxidation-reduction reactions and define the oxidant and reductant:

(1) $KMnO_4 + NaNO_2 + H_2SO_4(dil.) \rightarrow MnSO_4 + NaNO_3 +$

(2) $NaClO + KI + H_2SO_4(dil.) \rightarrow NaCl + I_2 +$

(3) $Cl_2 + KOH \rightarrow KClO_3 +$

(4) $I_2 + Cl_2 + H_2O \rightarrow HIO_3 +$

(5) $NO_2 + NaOH \rightarrow NaNO_2 +$

(6) $K_2Cr_2O_7 + H_2SO_4(dil.) + FeSO_4 \rightarrow Cr_2(SO_4)_3 +$

(7) $H_2S + H_2SO_3 \rightarrow S +$

(8) $KClO_3 \rightarrow O_2 +$

(9) $KClO_3 \rightarrow KClO_4 +$

(10) $HNO_2 \rightarrow NO +$

(11) $KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(12) $As_2S_3 + HNO_3 \rightarrow H_3AsO_4 + H_2SO_4 + NO +$

(13) $MnO_2 + HCl(conc.) \rightarrow$

(14) $Mg + HNO_3 \rightarrow Mg(NO_3)_2 + NH_4NO_3$

(15) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO +$

(16) $KI + H_2SO_4(conc.) \rightarrow I_2 + H_2S +$

2. Which of the following substances: Cl_2, PbO_2, $K_2Cr_2O_7$, $KMnO_4$, Na_2S, KI, KBr, $FeSO_4$, Na_2SO_3, $NaNO_2$ are only oxidants, only reductants, and which can act both as reductants and oxidants?

3. Using the ion-electron method, complete the following:

(1) $MnO_4^- + NO_2^- + H^+ \rightarrow Mn^{2+} + NO_3^- +$

(2) $Fe^{3+} + S^{2-} \rightarrow S + Fe^{2+}$

(3) $MnO_4^- + I^- + H^+ \rightarrow Mn^{2+} + I_2 +$

(4) $ClO^- + I^- \rightarrow IO_3^- + Cl^- +$

(5) $MnO_4^- + SO_3^{2-} + H^+ \rightarrow Mn^{2+} + SO_4^{2-} +$

(6) $MnO_4^- + NO_2^- + H^+ \rightarrow MnO_4^{2-} + NO_3^- +$

8.2. Direction of Oxidation-Reduction Reactions

4. Figure 21 shows the variation of ΔG_f° of antimony chlorides with temperature. The formation of which chloride, $SbCl_3$ or $SbCl_5$, is predominant in the interaction between Sb and Cl_2?

Experiment 1. Reaction between antimony and chlorine. (Use the hood!) Obtain chlorine in an apparatus shown in Fig. 22 by the action of concentrated hydrochloric acid on manganese dioxide. Fill a test tube with chlorine and stopper it. Fix the test tube in a stand and place antimony powder (heated preliminarily on a metal spatula) into it; explain the sparkling shower and dense smoke ($SbCl_3$: m.p., 73°C; b.p., —221°C; $SbCl_5$: m.p., 3°C; b.p., 140°C).

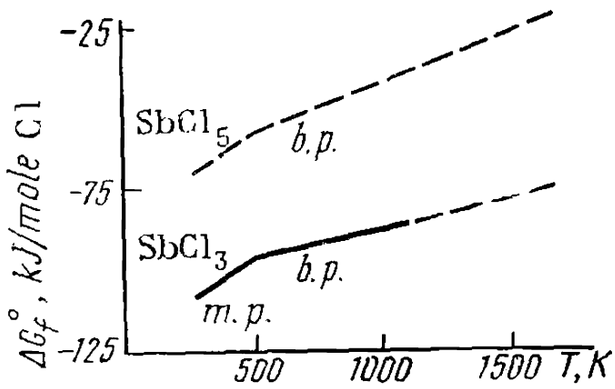


Fig. 21. Variation of ΔG_f° of antimony chloride with temperature (*m.p.* is melting point and *b.p.* is boiling point):
A continuous line shows the experimentally found values and broken lines show the calculated values

5. Calculate ΔH_{298}°, ΔS_{298}° and ΔG_{298}° of the reaction

$$2(NH_4)_2CrO_4(c) = Cr_2O_3(c) + 2H_3N(g) + N_2(g) + 5H_2O(g)$$

(a) What is the role of the enthalpy and entropy factors in this process?

(b) Is this process reversible?

(c) What elements change their oxidation state?

Experiment 2. Thermal decomposition of ammonium dichromate(VI). (Use the hood!). Place powdered crystals of $(NH_4)_2Cr_2O_7$ into a dry test tube, and fix it in the stand in the inclined position (with its mouth away from yourself and your mates). Heat carefully the upper layer until the reaction begins and discontinue heating. Explain the volcanic character of the reaction.

6. (a) Calculate ΔG_{298}° and determine the thermodynamic ability of the thermal decomposition of $Na_2SO_3(c)$ with the formation of $Na_2S(c)$ and $Na_2SO_4(c)$.

(b) What type of oxidation-reduction reactions is this process?

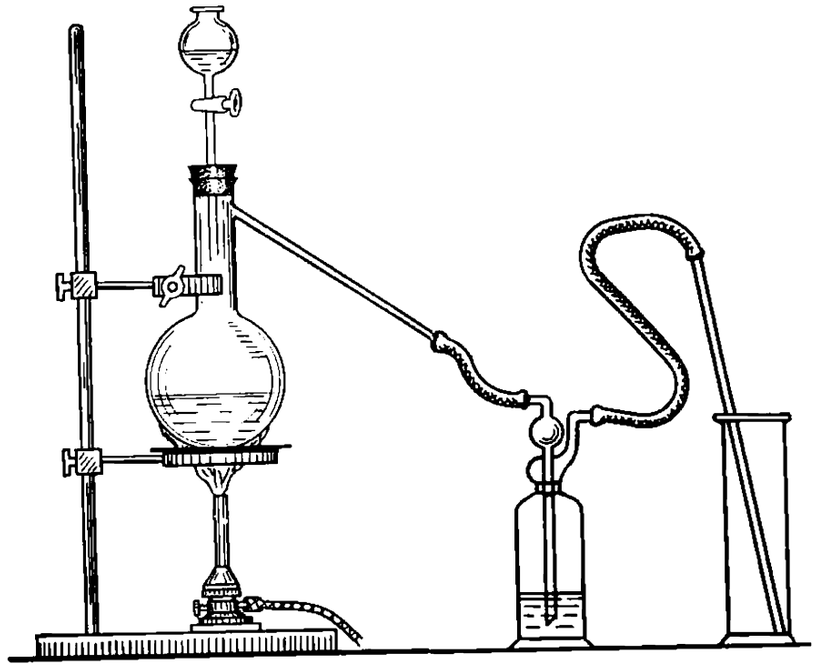


Fig. 22. Apparatus for obtaining gases (Cl_2, CO, SO_2 and others)

Experiment 3. Thermal decomposition of sodium oxysulphate (IV). (Use the hood!) Place about 0.5 g of $Na_2SO_3 \cdot 7H_2O$ into two separate test tubes. Keep one of them as a control. Fix the other one in a stand in the inclined position, heat for 5-6 minutes, and cool. Dissolve the contents of both test tubes in water and add 2-3 drops of cupric sulphate to each solution. Explain your observations remembering that the black precipitate is cupric sulphide.

7. Can the following process be realized:

$$Zn(c) + CuSO_4(sln) = ZnSO_4(sln) + Cu(c)?$$

Calculate the variation of the Gibbs free energy and the electromotive force of the voltaic cell under standard conditions.

Experiment 4. Voltaic cell. Place equal volumes of 1 *N* solutions of zinc sulphate and cupric sulphate into two separate beakers. Interconnect the solutions by a salt bridge (saturated solution of potassium chloride in agar-agar). Connect a zinc and a copper plate to a galvanometer. Immerse the plates into the solutions of $ZnSO_4$ (zinc) and $CuSO_4$ (copper): the galvanometer pointer deviates from its original position. Explain. Indicate the direction of currents of electrons in the outer circuit and of ions in the inner one.

8. (a) Use the values of $E^{\circ}_{M^{n+}/M}$ to arrange the metals in the electromotive series.

(b) What happens if we immerse an iron plate into a solution of cupric sulphate? Prove your answer by the standard electrode potentials of the corresponding systems.

Experiment 5. Comparing chemical activity of iron and copper. Degrease and etch (in hydrochloric acid) an iron plate and immerse it into a 1 *N* solution of cupric sulphate. Keep it in the solution for a while and remove. Explain your observations.

9. Use $E^{\circ}_{E/E^{n-}}$ values to make out the electrochemical series of nonmetals.

(a) How does the oxidation activity of the halogens vary with their increasing atomic number?

(b) Will a chemical reaction occur if chlorine water is added to (a) potassium iodide solution; (b) potassium fluoride solution?

Experiment 6. Comparing the chemical activity of chlorine and iodine. (Use the hood!) Add chlorine water, by drops, to potassium iodide solution. Explain your observations.

10. Can the Fe^{2+} ions be oxidized with the Sn^{4+} ions by the following reaction: $2Fe^{2+} + Sn^{4+} \rightarrow 2Fe^{3+} + Sn^{2+}$?

Experiment 7. Reaction between solutions of Fe(III) and Sn(II) compounds. Add a solution of a ferric salt to a solution of potassium thiocyanate or ammonium thiocyanate. Note the colour of the resultant solution. Then add, by drops, stannous chloride solution till the solution clears. In what direction and why will the equilibrium of the system

$$FeCl_3 + 3KCNS \rightleftarrows Fe(SCN)_3 + 3KCl$$

shift?

11. Will the oxidation-reduction reaction occur if a solution of ferric sulphate is mixed with a solution of (a) potassium iodide; (b) sodium bromide?

Experiment 8. Reaction between solutions of ferric salts and sodium iodide. Add NaI solution to an acidified ferric salt solution. Explain your observations. Try to see if a reaction occurs between solutions of a ferric salt and sodium bromide.

12. Which of the following systems:

$$Fe^{3+} + e^- = Fe^{2+} \qquad F_2 + 2e^- = 2F^-$$

$$Co^{3+} + e^- = Co^{2+} \qquad S + 2H^+ + 2e^- = H_2S$$

$$Pb^{4+} + 2e^- = Pb^{2+} \qquad I_2 + 2e^- = 2I^-$$

will be reductants if an acid solution of potassium manganate(VII) is used as an oxidant

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

Write the equations of the reactions.

Experiment 9. Reactions between potassium manganate(VII) and ferrous sulphate solutions. Add $FeSO_4$ solution to a solution of $KMnO_4$ acidified with sulphuric acid. Explain your observations.

Experiment 10. Reaction between potassium manganate(VII) and hydrogen sulphide solutions. (Use the hood!) Add hydrogen sulphide water to $KMnO_4$ solution acidified with sulphuric acid. Explain your observations.

13. Give oxidation-reduction potentials of the following half reactions

$HNO_2 + H^+ + e^- = NO + H_2O$ $\quad MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$

$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$ $\quad I_2(c) + 2e^- = 2I^-(sln)$

(a) Will the oxidation state of nitrogen change if $KMnO_4$ or KI solution acts on an acidified $NaNO_2$ solution?

(b) What properties, oxidizing or reducing, $NaNO_2$ shows in this reaction?

Experiment 11. Oxidizing properties of sodium nitrate(III). (Use the hood!) Add sodium nitrite solution to a potassium iodide solution acidified with dilute sulphuric acid. Note the evolving gas which gets brown on exposure to air. Note also the colour of the resultant solution. Prove experimentally that the evolving gas is iodine. Write the equation of the reaction.

Experiment 12. Reducing properties of sodium nitrate(III). (Use the hood!) Acidify potassium manganate(VII) solution with dilute sulphuric acid and add sodium nitrite solution. Explain your observations. Write the equation of the reaction.

14. Give the standard oxidation-reduction potentials of the half reactions:

in acid medium	$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$
	$SO_4^{2-} + 2H^+ + 2e^- = SO_3^{2-} + H_2O$
in neutral medium	$MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4OH^-$
	$SO_4^{2-} + 2H^+ + 2e^- = SO_3^{2-} + H_2O$
in alkaline medium	$MnO_4^- + e^- = MnO_4^{2-}$
	$SO_4^{2-} + H_2O + 2e^- = SO_3^{2-} + 2OH^-$

(a) Determine the thermodynamic probability of reactions between solutions of $KMnO_4$ and Na_2SO_3 in: (1) acid; (2) alkaline; (3) neutral medium.

(b) In what medium are the oxidizing properties of the ion MnO_4^- stronger?

Experiment 13. Reduction of the MnO_4^- ion in various media. Add dilute sulphuric acid into three separate test tubes containing potassium manganate(VII) solution. Add the same volume of water and concentrated alkali solution. Now add sodium sulphite(IV) Na_2SO_3 solution into each test tube. Explain your observations assuming that the Mn^{2+}-ion is formed in the acid medium, MnO_2 in the neutral medium and the MnO_4^{2-}-ion in the alkaline medium.

15. Calculate the potential of the system Fe^{3+}/Fe^{2+}, if the activity of Fe^{3+} is 0.1 mole/l and of Fe^{2+}, 5×10^{-3} mole/l.

16. (a) Calculate the potential of the system MnO_4^-/Mn^{2+} if: (1) $[H^+] = 1$ mole/l; (2) $[H^+] = 1 \times 10^{-2}$ mole/l and if $[MnO_4^-]/[Mn^{2+}] = 1$.

(b) Explain the variation of the $E_{MnO_4^-/Mn^{2+}}$ with pH of the medium (Fig. 23).

(c) At what pH can the ion MnO_4^- be reduced by the ions: (1) I^-; (2) Br^-; (3) Cl^-?

17. (a) What processes take place at the cathode and anode during the electrolysis of: (1) NaCl melt; (2) NaCl solution?

(b) Calculate the electromotive force which is required to decompose sodium chloride at 1100 K, if the ΔG_f° at 1100 K is —311 kJ/mole.

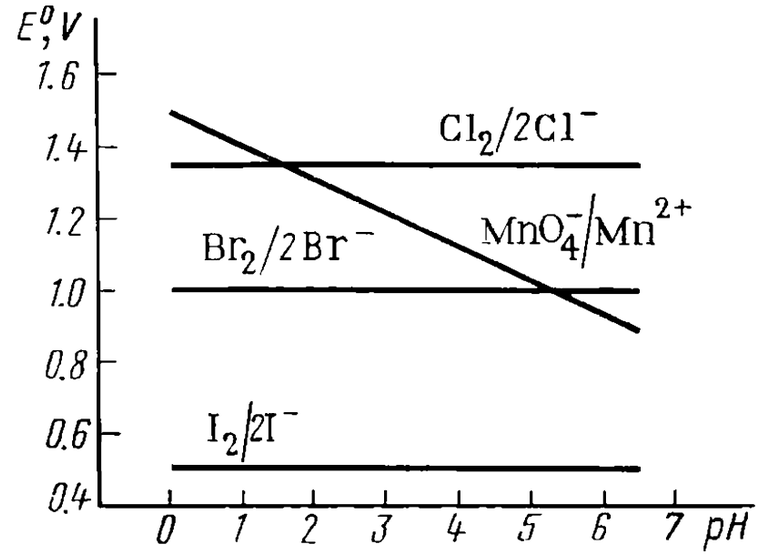


Fig. 23. Variation of potential of the system MnO_4^-/Mn^{2+} with pH

18. Make out equations of reactions that occur during electrolysis of a solution of potassium iodide at carbon electrodes. Prove your answer experimentally as instructed below.

Experiment 14. Electrochemical oxidation-reduction. Electrolysis of potassium iodide solution. Immerse graphite electrodes into an electrolyzer filled with a solution of potassium iodide and connect the circuit to a source of direct current. Add a few drops of phenolphthalein to the solution at the cathode. Explain the changing colour at the cathode and anode.

When the experiment is over, wash the anode with a solution of sodium thiosulphate, $Na_2S_2O_3$, to remove iodine, and then with distilled water. Keep the iodine residue in a special bottle.

PART TWO

CHEMISTRY OF ELEMENTS

I

s- AND *p*-ELEMENTS OF THE MENDELEEV PERIODIC SYSTEM

CHAPTER 1

p-Elements of Group VII

1.1. Atoms and Simple Substances

1. Show graphically the variation of the atomic radius, the first ionization energy and the electron affinity with the atomic number of the halogens. Explain the curves. Explain why the ionization energy does not decrease monotonously with increasing atomic number while the electron affinity first increases and then decreases?

2. (a) What is the ground oxidation state of the halogens? In what natural compounds do the halogens occur?

(b) What is the general principle used to obtain the halogens in industry and laboratory? What special conditions are required for obtaining fluorine?

(c) Give examples of reactions by which the halogens are obtained.

Experiment 1. Obtaining the halogens. (Use the hood!) (a) Place MnO_2 powder into a test tube provided with a gas outlet tube and add as much of concentrated HCl as to cover the MnO_2 layer. Heat the mixture carefully and examine the evolving gas using filter paper moistened with KI solution. Note the colour of the gas.

Collect chlorine into a dry test tube. While filling the test tube with chlorine it is necessary to lower the outlet tube to the bottom. Stopper the filled test tube and keep it for further experiments. Write the equations for the reactions of preparation and detection of chlorine.

(b) Put 2-4 crystals of KBr (KI) and an equal quantity of MnO_2 into a dry test tube. Add a few drops of concentrated H_2SO_4 and heat the mixture slightly. Explain your observations.

3. Figure 24 shows the variation of the potential energy of the system of two halogen atoms with the internuclear distance.

(a) Using the MO theory, explain why the dissociation energy of molecular Hal_2 is relatively low.

(b) How do the internuclear distance and the bond energy vary in the series F_2-Cl_2-Br_2-I_2? Explain.

4. Draw the enthalpy diagram and calculate the standard enthalpy of the formation of the gaseous ions F^-, Cl^-, Br^-, and I^-.

(a) How does the ΔH_f° of the ions vary in the series F^--I^-? Explain.

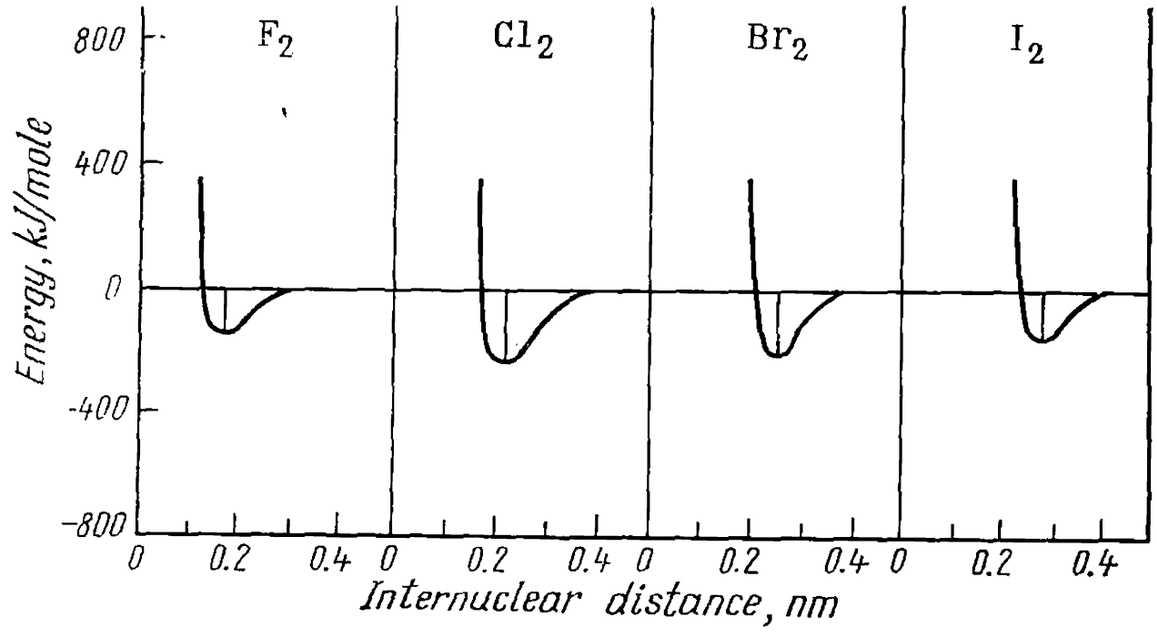


Fig. 24. Variation of potential energy of halogen molecules with the internuclear distance

(b) Compare the character of the variation in the subgroup of the halogen standard electrode potentials and ΔH_f of the Hal^- ions. How does the oxidizing activity vary in the halogen series?

5. Using the values of the standard electrode potentials of the halogens and the systems:

$$S + 2H^+ + 2e^- = H_2S$$

$$SO_4^{2-} + 2H^+ + 2e^- = SO_3^{2-} + H_2O$$

decide what reactions will occur if the following solutions are mixed: (1) hydrogen sulphide and chlorine water; (2) iodine and sodium oxysulphate(IV). Prove your answers experimentally.

Experiment 2. Oxidizing properties of the halogens. (Use the hood!)

(a) Place a few drops of chlorine water into a test tube containing hydrogen sulphide water. Explain your observations.

(b) Add, by drops, iodine water to Na_2SO_3 solution. Explain your observations.

6. Calculate the ΔH_{298}° of oxidation of red phosphorus by the halogens to phosphorus trihalides if the mean bond energies E_{PHal}, atomization energies of red phosphorus and of the halogens are

known:

	PF	PCl	PBr	PI
E_{PHal}, kJ/mole . . .	490	306	264	185

Compare the results with the tabulated data.

How can the high chemical activity of fluorine be explained and why does the oxidizing activity fall in the series F_2-Cl_2-Br_2-I_2?

Compare the oxidizing activity of Cl_2 and I_2 in the following experiments.

Experiment 3. Oxidation of phosphorus by chlorine (iodine). (Use the hood!) (a) Place powdered red phosphorus into a test tube containing chlorine. Explain your observations.

(b) Place a dry mixture of iodine and red phosphorus (about 1:6) into a dry test tube. Close the tube with a stopper with a gas outlet tube, fix it in a stand and heat slightly for 2-3 minutes. Explain your observations. Do not discard the reaction product.

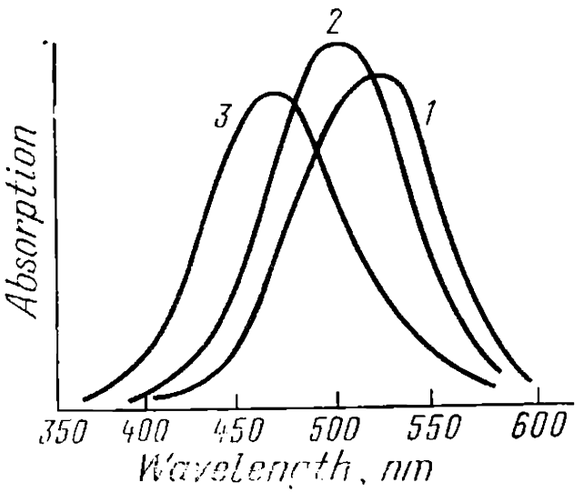


Fig. 25. Spectrum of iodine in various solvents:
1—in CCl_4; *2*—in C_6H_6; *3*—in $(C_2H_5)_2O$

7. The maximum absorption of iodine vapour and of iodine in CCl_4 solution (Fig. 25) is at about 520 nm.

(a) What is the colour of iodine in the vapour state and in the CCl_4 solution?

(b) Explain why the colour of iodine vapour is the same as that of iodine solution in CCl_4?

Experiment 4. Colour of iodine vapour and iodine solution in CCl_4. (Use the hood!) Place 1-2 crystals of iodine into two dry test tubes. Heat one test tube to iodine vapour and add CCl_4 to the other test tube. Explain your observations.

8. Add a substance (A) whose molecules donate electron pairs to iodine solution in CCl_4: intermolecular complexes of the $I_2 \cdot A$ type are formed. The absorption bands of the solution are displaced toward shorter wavelengths and the solution colour changes (Fig. 25).

Using the diagram of the orbitals of the intermolecular complex $I_2 \cdot A$ (Fig. 26), the data on the enthalpy of the reactions of formation of these complexes and the absorption spectra (Fig. 25) predict the maximum change in the colour of iodine in the following solvents:

	$I_2 \cdot C_6H_6$	$I_2 \cdot CH_3OH$	$I_2 \cdot (C_2H_5)_2O$	$I_2 \cdot (C_2H_5)_3N$
$\Delta H^\bullet_{298}$, kJ/mole . . .	—5.9	—7.9	—18.0	—50.2

Experiment 5. Iodine dissolution in different solvents and colour of the solutions. Try iodine for solubility in benzene, alcohol, ethyl ether and triethylamine. Explain the different colour of the solutions.

1.2. Compounds with the Oxidation State of Halogens —1

9. Figure 27 shows the potential energy curves for the formation of the hydrogen halides from atoms.

(a) How does the configuration of the "potential well" vary with the force constant k and the frequency of valency oscillations $\tilde{\nu}$ of a HHal molecule?

	HF	HCl	HBr	HI
k, N/m	966	516	412	297
$\tilde{\nu}$, cm^{-1} . . .	3960	2885	2560	2230

(b) How does the bond energy vary in the series HF-HCl? Explain.

10. Calculate the ΔH° of the reaction $HHal(g) = H^+(sln) + Hal^-(sln)$, if the energy of the HHal molecule dissociation to

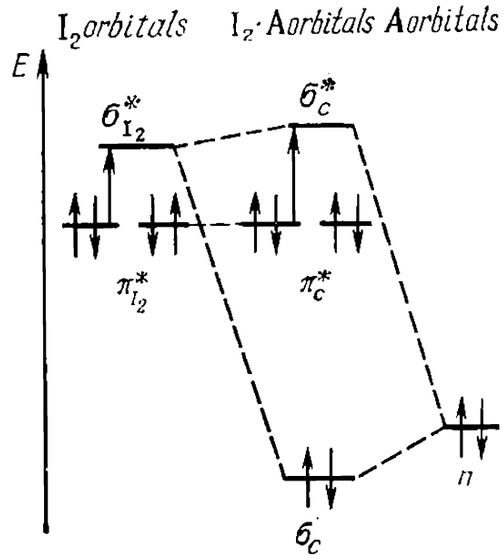


Fig. 26. Molecular orbitals of the $I_2 \cdot A$ complex

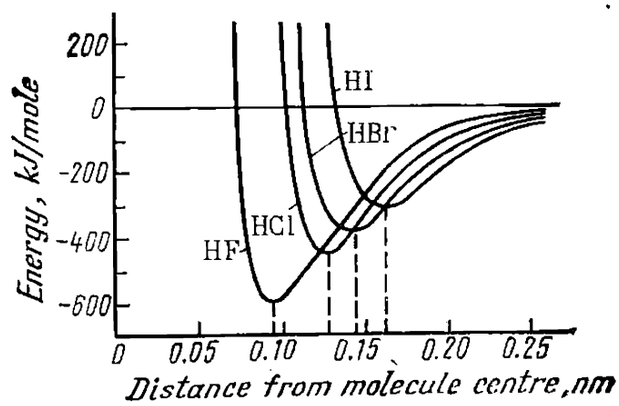


Fig. 27. Potential energy of the system H + Hal and its variation with the internuclear distance

atoms, the electron affinity of Hal and hydration energy of Hal^- are known and the energy of the transformation of H(g) into $H^+(sln)$ is 204 kJ/mole. What is the main cause of the variation of acid strength in the series HF-HCl-HBr-HI? Explain.

11. Calculate the ΔG°_{298} of the reaction of formation of AgHal(c) and $CaHal_2(c)$ from ions in solution.

(a) How does the solubility change in the series F^--Cl^--Br^--I^-? Compare the character of the variation of ΔG and SP in the series. SP values are not available for all halides. Why?

(b) What cations should be used to detect the floride ions and the anions of the other halogens in solution?

Experiment 6. Sparingly soluble halides (qualitative tests for the halide ions). Test the action of silver(I) and lead(II) ions on the

halide ion. Note the colour of the precipitate formed. Write the reaction equations.

12. Calculate the ΔG°_{298} of the reactions between HHal(g) and H_2SO_4(l) in which free halogen, SO_2(g) and H_2O(l) are formed.

(a) What hydrogen halides are suitable for the purpose?

(b) How does the reducing power vary in the series HF-HCl-HBr-HI? Explain your answer.

(c) What hydrogen halides can be produced by the reaction of the corresponding halides of sodium (or potassium) with concentrated H_2SO_4? Prove your answer experimentally.

Experiment 7. Preparing hydrogen fluoride and glass etching. (Use the hood!) Coat a glass plate with paraffin and scratch out a character or some other figure on the coat (to reach glass).

Take a porcelain crucible and place 1 g of CaF_2 in it. Add 2-3 ml of concentrated H_2SO_4 (density 1.84 g/cc) and cover the crucible immediately with the glass, the paraffin coat down. Heat the crucible gently over a burner for 3-5 minutes. Cool the crucible, take the glass and remove the paraffin. Observe the result of the etching process. Write the reactions of obtaining HF and glass etching.

Experiment 8. Preparing hydrogen chloride and hydrochloric acid. (Use the hood!) Place NaCl into a test tube provided with a gas-outlet tube. Add several drops of concentrated H_2SO_4 and heat the mixture slightly. Put alternately moist litmus paper and a glass rod wetted with concentrated ammonia solution to the outlet tube. Observe the reaction.

Pass the evolving gas into a test tube containing water without immersing the outlet tube. Use qualitative tests to identify hydrochloric acid.

Experiment 9. Comparison of the reducing properties of hydrogen halides. (Use the hood!) Put KBr and KI into two separate test tubes. Add a few drops of concentrated sulphuric acid into each of them and heat slightly. Note the colour of the evolving vapours. Smell them very carefully and try with litmus. Write down the reaction equations.

13. Characterize the acid-base properties of NaCl and $SbCl_5$, KF and PF_5. Write the equations of their hydrolysis and the interaction of the pairs.

Experiment 10. Hydrolysis of the halides. Determine the medium of NaCl and $AlCl_3$ solutions. Explain your observations.

Experiment 11. Obtaining hydrogen iodide by hydrolysis. (Use the hood!) Add a few drops of water to a test tube containing PI_3 obtained in Experiment 3. Try the action of the evolving gas on moist litmus paper. Explain your observations.

14. Write the reaction equations for the formation of $NaMgF_3$(c), Na_3AlF_6 (c) and Na_2SiF_6 (c) from binary fluorides. The ΔG°_{298} of the reactions are —14 kJ, —31 kJ and —51 kJ per 1 mole of NaF, respectively. Explain the variation of the acid-base properties in the

series $NaF(c)$-$MgF_2(c)$-$AlF_3(c)$-$SiF_4(l)$. How does this variation agree with the changing ΔG?

Experiment 12. Formation of halide complexes. Add, by drops, a solution of potassium iodide to a solution of bismuth(III) nitrate until a precipitate falls out. Add excess KI solution to dissolve the precipitate. Make your conclusions on the acid-base properties of the interacting iodides.

1.3. Compounds with the Halogens in the Positive Oxidation State

15. Below follow examples of binary halogen compounds and the corresponding anion complexes:

Cl_2O	ClF	BrF_3	IF_5	Cl_2O_7	IF_7
ClO^-	ClF_2^-	BrF_4^-	IF_6^-	ClO_4^-	IF_8^-

(a) Describe the structure of ClF, ClF_3 and ClF_5 molecules (from the point of view of the hypervalent bond concept). Explain the different length of bonds and bond angles.

(b) What are the acid-base properties of the binary compounds with the halogens in the positive oxidation state? Write the reaction equations.

16. The constants of hydrolysis of the halogens are as follows:

	Cl_2	Br_2	I_2
K_h	3×10^{-4}	4×10^{-9}	5×10^{-13}

(a) Write the equation and the equilibrium constant for the reaction between the halogens and water.

(b) In which direction will the equilibrium shift if acid or alkali is added to the aqueous halogen solutions?

(c) What is the difference between the action of chlorine on cold and hot alkali solutions?

(d) How does the attitude of fluorine to water and alkali differ from that of the other halogens?

Experiment 13. Obtaining sodium hypochlorite. (Use the hood!) Pass chlorine gas through a cooled alkali solution. Test the solution for the presence of the chloride ion. Explain your observations.

Experiment 14. Obtaining potassium hypochlorite. (Use the hood!) Pass chlorine into a hot concentrated solution of potassium hydroxide for 3-5 minutes. Cool the solution. Explain precipitation of crystals.

Experiment 15. Action of alkalis on bromine and iodine. (Use the hood!) Add, by drops, a solution of an alkali into a test tube containing liquid bromine (or iodine crystals). The solution discolours. Now add dilute H_2SO_4 to acid reaction and a few drops of benzene. Shake the mixture. Explain the phenomena observed.

17. Compare the standard oxidation-reduction potentials of the systems

$$ClO_n^- + nH_2O + 2ne^- = Cl^- + 2nOH^- \qquad (n = 1, 3, 4)$$

and pK of acids corresponding to the hypochlorite ions.

(a) How does the oxidizing power vary in the series ClO^--ClO_2^--ClO_3^--ClO_4^-?

(b) What effect does the effective charges δ_0 on the oxygen atom in the ion ClO_n^-

	ClO^-	ClO_2^-	ClO_3^-	ClO_4^-
δ_0	−1	−0.715	−0.43	−0.359

produce on the strength of the H—O bond? What effect does it have on the strength of the oxyacids of chlorine in the series?

Experiment 16. Comparison of the oxidizing power of oxychlorate(I) and oxychlorate(V) ions. Compare the reaction of the KI solution with solutions of $KClO_3$ and KClO. Explain your observations.

18. $HClO_3$ does not exist in the free state, while $KClO_3$ is quite stable.

(a) Explain this fact.

(b) Add KI solution to an acidified and neutral $KClO_3$ solution: will the reactions occur? Prove your answer by the E°_{298} values of the corresponding half reactions.

Experiment 17. (a) Effect of medium on the oxidizing power of the oxychlorate(V) ion. Place $KClO_3$ solution into two test tubes. Add KI solution. Now add dilute sulphuric acid into one of them. Compare and explain the results of the experiment.

(b) Oxidation of concentrated hydrochloric acid by oxychlorate(V). Add concentrated hydrochloric acid into a test tube containing potassium chlorate. Identify experimentally the evolving gas.

19. Using the E° values of the corresponding half reactions predict the result of the reactions between the following: (1) KI solution and excess chlorine water; (2) HIO_3 and Na_2SO_3 solutions. Check your answer by carrying out the following experiments.

Experiment 18. Formation of iodic acid and its oxidizing properties. (Use the hood!) (a) Add 2-3 drops of KI solution and benzene into a test tube containing water. Then add, by drops, chlorine water. The solution first colours and then clears. Explain.

(b) Add, by drops, Na_2SO_3 solution into a test tube containing HIO_3 solution. The colour first develops and then disappears. Explain.

20. Give examples of disproportionation and intramolecular oxidation-reduction reactions of oxyhalides.

Experiment 19. Catalytic decomposition of chloride of lime. Prepare a mixture of chloride of lime with CuO or NiO. Heat the mixture carefully in the test tube. Prove that the evolving gas is oxygen. Explain your observations.

21. The linear structure of the ions $BrCl_2^-$, ICl_2^-, Cl_3^-, Br_3^-, I_3^- has been proved experimentally. The central atoms bear a positive effective charge, while the peripheral ones are charged negatively.

(a) Describe the structure of the ions using the MO theory.

(b) How does the stability of Hal_3^- ion vary in the series Cl_3^--Br_3^--I_3^- if the equilibrium constants of the reaction $Hal^- + Hal_2 \rightleftharpoons Hal_3^-$ are as follows:

	Cl_2	Br_2	I_2
K	0.2	16	700

Experiment 20. Formation of potassium diiodoiodate(I). Place a few crystals of iodine into a test tube containing water and boil. Decant the solution and keep it as a standard. Add concentrated KI solution to undissolved crystals. Compare the colour of the solutions.

22. Liquid halogen halides are supposed to undergo autoionization, for example:

$$BrF_3 + BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-; \quad IF_5 + IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

Write the equations of the reactions of obtaining $KBrF_4$ and $(BrF_2)SbF_6$, KIF_6 and $(IF_4)SbF_6$ and explain them from the point of view of acid-base reactions.

23. It has been proved experimentally that $KClO_4$ decomposes at about 400°C; $HClO_4$ and Cl_2O_7 explode on heating; dilute $HClO_4$ solutions are quite stable; ClO_3F is thermally stable. Explain the different stability of the mentioned compounds.

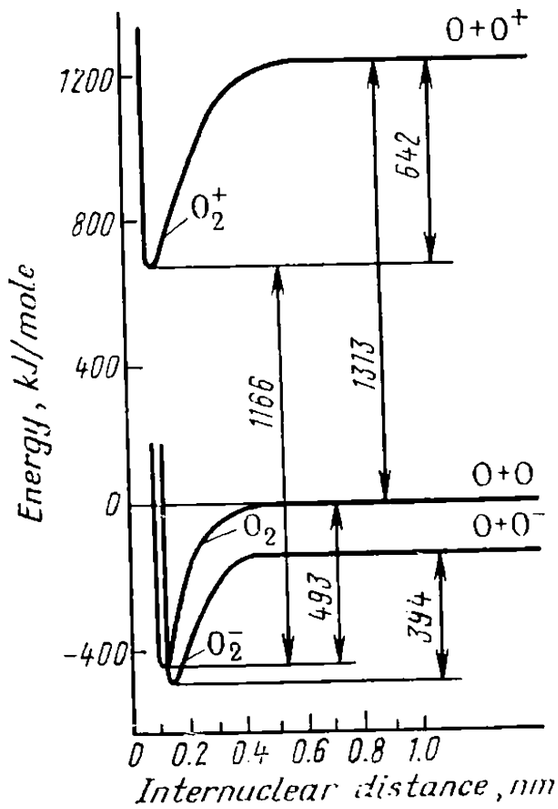


Fig. 28. Variation of potential energy of O_2, O_2^+ and O_2^- with the internuclear distance

CHAPTER 2

p -Elements of Group VI

2.1. Oxygen

1. Show graphically the energy diagram of the orbitals and give electron configurations for the ground states of O_2 molecule and molecular O_2^+-, O_2^-- and O_2^{2-}-ions.

What is the dissociation energy and the internuclear distance of O_2, O_2^+ and O_2^- (Fig. 28)? How does the variation of these values in the series O_2^+-O_2-O_2^- relate to the variation of distribution of electrons in orbitals and the order of bonding?

2. (a) Explain the variations of the force constant and the frequency of valency oscillations in the series O_2-O_2^--O_2^{2-}:

	O_2	O_2^-	O_2^{2-}
k, N/m	1154	559	290
$\tilde{\nu}$, cm^{-1}	1555	1145	842

(b) How and why do the ionization energies vary in the transition of the oxygen atom to the oxygen molecule?

3. Calculate the ΔG°_{298} of the decomposition of 1 mole of $KClO_3$(c) and Na_2SO_4(c), if oxygen is liberated and KCl(c) and Na_2SO_3(c) are formed.

(a) Which of these compounds is less thermally stable and can be used to obtain oxygen?

(b) What type of oxidation-reduction reactions is thermal decomposition of $KClO_3$, $KMnO_4$ and KNO_3?

Experiment 1. Preparing oxygen by decomposition of salts. Oxidizing properties of oxygen. (Use the hood!) Obtain oxygen by decomposing potassium oxychlorate(V) in the presence of a catalyst (MnO_2) and collect it in three cylinders. Put burning red phosphorus, sulphur and a red-hot iron chip into each cylinder. Explain your observations.

4. Effective charges δ_0 on the oxygen atom of oxides of the elements of the 2nd and 3rd periods are given below:

	Li_2O	BeO	B_2O_3	CO_2	N_2O_5		
δ_0 . .	—0.80	—0.35	—0.24	—0.11	—0.05		
	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
δ_0 . . .	—0.81	—0.35	—0.31	—0.23	—0.13	—0.06	—0.01

(a) Compare the character of the variation of the effective charge on the oxygen atom and of the chemical nature of the oxides in the period.

(b) Illustrate the properties of basic, amphoteric and acid oxides by the appropriate reactions.

(c) Write down the equations for the reactions of formation of $NaAlO_2$(c), Na_2SiO_3(c), Na_3PO_4(c), Na_2SO_4(c) and $NaClO_4$(c) from the oxides with reference to 1 mole of Na_2O and calculate their ΔG°_{298}. How do the acid-base properties of the oxides vary with the variation of the ΔG°_{298} values in the series of these reactions?

Experiment 2. Action of water on oxides. Pour distilled water into two test tubes. Add calcium(II) oxide into one of them and phosphorus(V) oxide into the other. Will a reaction occur? What is the medium of the resultant solutions?

5. Compare the structure of water in the different states of aggregation.

(a) Explain the appreciable changes in the frequency of valency oscillations of atoms in the H_2O molecule during transition of water

from the gaseous to the condensed state (crystal or liquid):

	H_2O (g)	H_2O (l)	H_2O (c)
$\tilde{\nu}$, cm^{-1} .	3655	3219	3400

(b) Why is ice lighter than water and why does the volume of water decrease on heating from 0 to 4°C?

(c) Explain the property of water to form clathrates. Give examples of the "gas hydrates".

Experiment 3. Abnormal properties of water. Pour distilled water into a dilatometer (an apparatus for experiments on the expansion of liquids on heating, Fig. 29) and close it with a stopper through which a graduated capillary tube is passed. Make sure that there are no air bubbles in the water. Place the bulb of the apparatus deep into thawing snow. Allow the water to cool to 0°C (for about 30 minutes) and pull the dilatometer from the snow. (Do not remove snow from the bulb if any sticks to its walls.) Keep it in the air and watch the liquid level in the capillary tube for 20-30 minutes. The volume of water changes on heating. Explain.

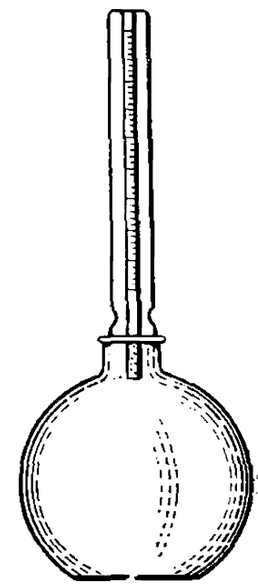


Fig. 29. Dilatometer

Experiment 4. Obtaining chlorine hydrate. (Use the hood!) Pass chlorine gas into water in a test tube placed on ice until crystals precipitate. Hold the test tube in the hand to warm it. Explain your observations. Add carbon tetrachloride to the solution and shake the mixture. Explain the colour of the carbon tetrachloride layer and that of the water.

6. The frequency of the valency oscillations $\tilde{\nu}_1$ of the bond O—H in a free H_2O molecule is 3655 cm^{-1}, but in aquo complexes it is lower. For example, in $CuSO_4 \cdot 5H_2O$, $\tilde{\nu}_1$ is 875 cm^{-1}. Explain.

Experiment 5. Formation of aquo complexes. Obtaining crystal hydrate $CuSO_4 \cdot 5H_2O$. Place about 1 g of anhydrous cupric sulphate into a test tube and add 5-10 ml of distilled water in small portions. Explain your observations. Transfer the solution into a porcelain dish and evaporate to halve its volume. Cool the solution and separate the precipitated crystals on a Büchner funnel.

7. It has been proved experimentally that the d_{O-O} bond length in KO_2 is 0.128 nm but in Na_2O_2 and BaO_2 it is 0.149 nm.

(a) Which of these compounds is superoxide and which is peroxide?

(b) How do these compounds react with water? Write the equations of the hydrolysis reactions.

(c) What is the charge (positive or negative) on the grouping O_2 in the compounds O_2F_2, $O_2[PtF_6]$ and $[V(O_2)_4]^{3-}$, if their d_{O-O}

bond lengths are 0.121 nm, 0.117 nm and 0.14 nm respectively (see Problem 1)?

Experiment 6. Hydrolysis of sodium peroxide. Place a pinch of sodium peroxide into a test tube filled with water. What gas is evolved? What compounds are formed in the solution? Explain your observations. To accelerate the process, use a catalyst (MnO_2).

Experiment 7. Obtaining hydrogen peroxide from barium peroxide. Pour about 5 ml of 2 *N* sulphuric acid into a beaker and cool it in ice or snow. Add 1 g of barium peroxide. Stir the mixture with a glass rod for 4-5 minutes. Separate the solution from the precipitate and add potassium iodide solution to see if hydrogen peroxide has formed.

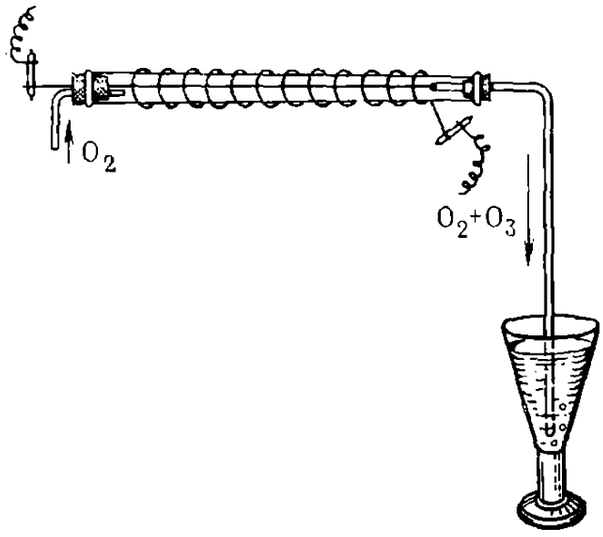


Fig. 30. Ozonator

8. What happens if the following solutions are mixed together: (1) acidified solutions of potassium tetraoxymanganate (VII) and hydrogen peroxide; (2) acidified solutions of potassium iodide and hydrogen peroxide?(3) What happens if hydrogen peroxide solution is heated?

Prove your answer by giving E° of the corresponding half reactions and by carrying out the following experiments.

Experiment 8. Oxidation-reduction properties of hydrogen peroxide. (a) Add a solution of hydrogen peroxide to a solution of potassium iodide acidified with an equal volume of sulphuric acid. Explain your observations.

(b) Add hydrogen peroxide solution to potassium tetraoxymanganate (VII) solution acidified with sulphuric acid. Explain your observations.

(c) Identify the gas which evolves on heating hydrogen peroxide. A catalyst (MnO_2) can be used to accelerate the reaction.

9. It has been established experimentally that the ozone molecule O_3 is diamagnetic: its valency angle $\angle$ OOO is 116°45′, the electric dipole moment μ is 0.52 C·m, and the d_{O-O} bond length is 0.128 nm.

(a) Explain the structure of the ozone molecule O_3.

(b) What is ΔG_f° of ozone? What conditions are necessary to obtain ozone from oxygen? Why?

(c) Compare the oxidizing power of O_3, O_2 and H_2O_2 by the values of the E°_{298} of the corresponding half reactions. Compare the thermodynamic probability of the reactions of potassium iodide solution with oxygen and ozone.

Experiment 9. Obtaining ozone. Oxidizing properties of ozone. Pass oxygen slowly through an ozonator (Fig. 30). Switch on electric current. Put a beaker filled with potassium iodide solution con-

taining a few drops of starch solution to the ozonator outlet tube. (Do not immerse the tube end into the solution.) The development of blue colour in the solution demonstrates the oxidizing properties of ozone. Explain your observations.

10. Write structural formulas of the following molecules: OF_2, O_2F_2, ClO_3F, NO_3F. Explain the high oxidizing properties of these compounds.

2.2. Sulphur

11. The energies of the single bonds O—O and S—S are 138 kJ/mole and 213 kJ/mole.

(a) Explain the difference between the energies of the bonds O—O and S—S and the tendency of sulphur to form homochains.

(b) What combinations of atoms form sulphur molecules? What type of molecules is the most stable?

(c) What structure units form crystals of rhombic, monoclinic and plastic sulphur?

12. Calculate the heat of the polymorphic conversion of monoclinic sulphur into rhombic if the heats of combustion of monoclinic and rhombic sulphur are 296.83 kJ/mole and 297.21 kJ/mole respectively.

What modification of sulphur is most stable in normal conditions?

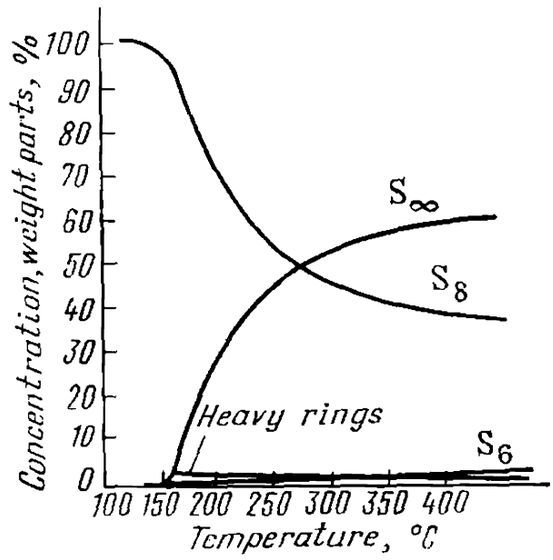


Fig. 31. Phase diagram of molten sulphur

Experiment 10. Obtaining rhombic sulphur. (Use the hood. Keep away from open flame!) Place 4-5 ml of CS_2 into a dry test tube and add sulphur powder by little portions to saturate the solution. Place a drop of the solution on a slide. Put a cover glass atop and watch the growth of crystals in a microscope (or a magnifying glass). Draw the crystals.

Experiment 11. Obtaining monoclinic sulphur. (Use the hood!) Melt slowly sulphur powder in a porcelain crucible. Allow the crucible to cool meanwhile watching the growth of a crystal crust. When the crust circle almost closes in the centre pour quickly the molten sulphur into a beaker filled with water. Examine the crystals in the crucible through a magnifying glass and draw them. Compare the shapes of the crystals obtained in Experiments 10 and 11. Explain the differences.

Dissolve 2-3 crystals obtained in CS_2 on a watch glass. Allow the solvent evaporate and examine the shape of the newly formed crystals. Give your explanations.

13. Using the diagram (Fig. 31) determine the regions of existence of the S_8 and S_∞ molecules.

Experiment 12. Polymorphic conversion of sulphur. (Use the hood!) Heat sulphur slowly in a dry test tube. Note that a highly mobile yellow liquid forms at the beginning of melting of sulphur (rhombic or monoclinic). On further heating (160°C) the liquid darkens and becomes more viscous. At 200°C it becomes red-brown and as viscous as pitch. On further heating (over 250°C) the liquid becomes more mobile again. Then, at 444.6°C, sulphur boils. As the temperature increases the colour of its vapour changes from orange-yellow to straw-yellow. Explain your observations using the diagram in Fig. 31.

Experiment 13. Obtaining plastic sulphur. (Use the hood!) Half fill a test tube with lumps of sulphur and heat slowly over a burner. Observe melting and the subsequent change in the colour and viscosity of sulphur. When sulphur begins boiling pour it in a thin jet into a crystallizer with cold water. (If sulphur gets on flame, disregard it and continue pouring. Stopper the test tube to quench the flame.) Take the obtained mass from the water and dry it between sheets of filter paper. Try the sulphur for extension. Note the change in properties of plastic sulphur in 1-2 hours.

14. (a) Give examples of the reactions in which sulphur acts as an oxidant and a reductant. Prove that the reactions are realizable, using the values of E°_{298} of half reactions.

(b) What conditions favour the disproportionation reactions of nonmetals?

Experiment 14. Disproportionation of sulphur. Add concentrated solution of alkali to sulphur powder in a crucible. Boil the mixture for 10 minutes. Using a paper wetted with $Pb(NO_3)_2$ solution prove the presence of the sulphide ion in the solution.

15. Will sulphur act as a reductant in the reaction with concentrated nitric acid? Prove your answer by E°_{298} values of the corresponding half reactions.

Experiment 15. Oxidation of sulphur with concentrated nitric acid. (Use the hood!) Place a lump of sulphur in a crucible filled with concentrated nitric acid. Boil for 5-7 minutes, adding new portions of nitric acid as it decomposes. Cool the crucible and dilute its content with water. Prove experimentally the presence of the SO_4^{2-} ions in the solution.

Experiment 16. Oxidizing properties of sulphur. (Use the hood!) Mix thoroughly zinc dust with two weights of sulphur flowers, place the mixture on a sheet of asbestos and touch it with a hot glass rod. Explain the flash.

16. Give examples of sulphides of the following groups: (1) soluble in water; (2) insoluble in water but soluble in dilute acids; (3) insoluble in acids; (4) insoluble in water or acids but soluble in solutions of basic sulphides; (5) unstable in aqueous solutions (completely hydrolyzing).

(a) Write the reactions of obtaining sulphides of each group.

(b) How can the ions K^+, Mn^{2+}, Ni^{2+} contained in one solution be separated by the sulphide method? Write the equations of the reactions.

Experiment 17. Obtaining sulphides and their solubility. (Use the hood!) Place solutions of salts of K^+, Fe^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Sb^{3+} and Cu^{2+} in test tubes and add hydrogen sulphide solution. Precipitate falls out in some test tubes.

Add $(NH_4)_2S$ solution to the solutions from which H_2S did not precipitate any substance. Precipitate falls out from some solutions again. What sulphides are soluble in water?

Add excess $(NH_4)_2S$ solution to the Sb_2S_3 precipitate. Explain the dissolution of the precipitate. Write the equations of the reactions.

17. Calculate the ΔG for the reactions between Al^{3+} (sln) and S^{2-} (sln) in an aqueous solution with the formation of the Al_2S_3(c) and $Al(OH)_3$(c) respectively. Which of these processes is more probable from the point of view of thermodynamics?

Experiment 18. Complete hydrolysis of sulphides. Add $(NH_4)_2S$ solution to a solution containing the Al^{3+} ions. Identify the precipitate experimentally.

18. The frequency of valency oscillations of the S—H bond of gaseous hydrogen sulphide is 2615 cm^{-1} and that of solid hydrogen sulphide is 2532 cm^{-1}.

(a) The frequency of valency oscillations of the S—H bond varies less significantly than that of the O—H bond during similar conversion of hydrogen oxide (see Problem 5). Explain why.

(b) Compare the boiling and melting points of hydrogen sulphide and water. Explain the character of the variation of these temperatures in the transition from H_2O to H_2S.

19. What is the general principle underlying the process of obtaining gases whose solutions are acids?

Experiment 19. Obtaining hydrogen sulphide. (Use the hood!) Place a small amount of ferrous sulphide in a test tube and add dilute hydrochloric acid. Close the test tube with a stopper with a gas outlet tube. Prove that the evolving gas is hydrogen sulphide using filter paper wetted with $Pb(NO_3)_2$ solution.

20. What reactions take place when hydrogen sulphide is passed through: (a) a solution of concentrated nitric acid; (b) a solution of potassium oxymanganate (VII); (c) chlorine water?

Prove your answer by E°_{298} of the corresponding half reactions.

Experiment 20. Reducing properties of hydrogen sulphide. (Use the hood!) Add hydrogen sulphide water to a strongly dilute and acidified solution of potassium permanganate. The solution becomes cloudy. Explain.

21. Sulphur is soluble in concentrated solutions of sulphides of alkali and alkaline earth metals. Explain why.

Experiment 21. Obtaining sodium polysulphide. (Use the hood!) Place 0.5 g of fine powder of sulphur (wetted with alcohol) into a

test tube containing 5-10 ml of concentrated sodium sulphide solution and boil the mixture carefully until the solution colour changes. Separate the obtained solution from unreacted sulphur by centrifuging. Transfer the solution separated from the precipitate into a test tube and keep for use in the next experiment.

Experiment 22. Obtaining hydrogen polysulphides and their decomposition. (Use the hood!) Place sodium polysulphide solution into a test tube and add, by drops, a 2 *N* solution of hydrochloric acid to acid reaction (litmus). Explain the appearance of colloidal precipitate.

22. Describe the structure of SF_4, SCl_4, SO_2, $SOCl_2$, SO_3^{2-}.

(a) How do dipole moments agree with the structure of molecules?

(b) What are the acid-base properties of halides, oxyhalides, and oxides of sulphur (IV)? Give equations of the corresponding reactions.

23. Calculate the ΔG°_{298} for the reactions of oxidation by oxygen of SO_2(g) to SO_3(c) and SO_3^{2-}(sln) to SO_4^{2-}(sln), with reference to one mole of O_2.

(a) Which of these processes is more likely to occur under ordinary conditions?

(b) Under what conditions is SO_2 oxidized to SO_3 in industry?

Experiment 23. Obtaining sulphur dioxide and its solubility in water. (Use the hood!) Assemble an apparatus shown in Fig. 22. Place anhydrous sodium sulphite into a Würtz flask and 40 per cent sulphuric acid into a dropping funnel. Add sulphuric acid to the sodium sulphite by small portions only after the previous portion of the acid has reacted. Control liberation of sulphur dioxide either by adding sulphuric acid or by heating the flask. Collect the liberated SO_2 in a cylinder and cover it with a glass plate. Fill water into a crystallization dish and add 2-3 drops of ammonia solution and 2-3 drops of blue litmus solution. Turn the cylinder upside down into the water in the crystallization dish and remove the glass plate under water. Observe the reaction and explain it.

Experiment 24. Catalytic oxidation of sulphur dioxide. (Use the hood!) Place 30-50 ml of sulphur dioxide solution into a 500-1000 ml bottle. Shake thoroughly the bottle, incline it slightly and put a red-hot platinum plate or spiral into it, a white smoke appears. Explain.

Experiment 25. Oxidation of SO_3^{2-} ion with sulphur. (Obtaining sodium thiosulphate.) Place about 1 g of sulphur powder wetted with a few drops of ethyl alcohol into a porcelain dish. Add 10 ml of sodium sulphite solution. Boil the mixture for 5 minutes over a low flame stirring it with a glass rod. Separate undissolved sulphur on a filter. Act with dilute hydrochloric acid on a portion of the solution. Explain your observations. Keep the remaining solution for further experiments.

24. (a) In what direction will a reaction proceed if bromine water is added to potassium oxysulphate(IV) solution?

(b) What is the product of the reaction between sodium oxysulphate(IV) and hydrogen sulphide solutions?

(c) What type of oxidation-reduction process occurs when sodium oxysulphate(IV) is heated?

Give E° data of the corresponding half reactions. Prove your answer by carrying out the following experiments.

Experiment 26. Oxidation-reduction properties of SO_3^{2-} ion. (a) Add, by drops, bromine water to sulphur dioxide solution. Identify experimentally the reaction products.

(b) Add H_2S solution to Na_2SO_3 solution acidified by sulphuric acid. Explain your observations.

(c) Fix a dry test tube containing 3-4 crystals of sodium sulphite in a stand and heat over a burner for 4-5 minutes. Then cool the test tube and dissolve its contents in water. Test the formed solution for the sulphide ion.

25. Describe the structure of halide, oxyhalides, and oxide of sulphur(VI) and of the corresponding anion complexes of sulphur(VI).

(a) What coordination number is most characteristic of sulphur(VI)? Why is the SO_3 molecule unstable under ordinary conditions? Describe the structure of the ice-like and asbestos-like modifications of sulphur trioxide.

(b) Give examples of reactions illustrating the acid-base properties of the fluoride, oxyhalides, and oxide of sulphur (VI).

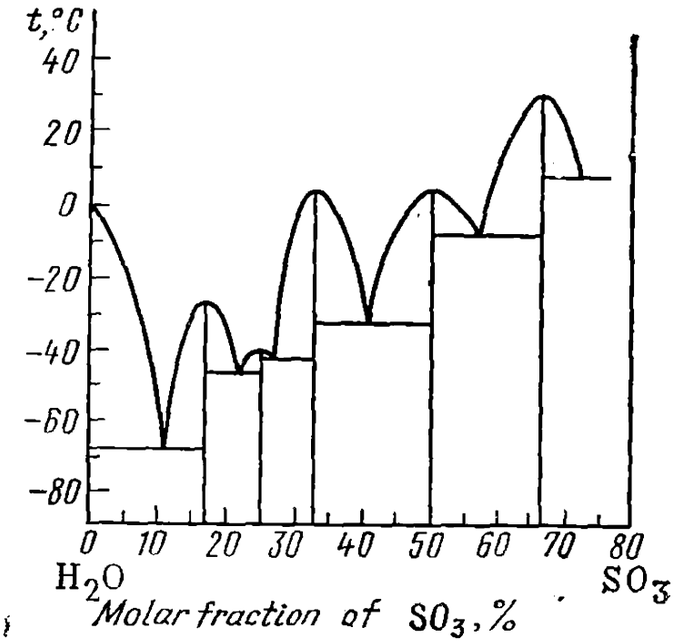


Fig. 32. Phase diagram of the SO_3-H_2O system

(c) The reaction of hydrolysis of SF_6 ($\Delta G^\circ_{298} = -460$ kJ/mole) is thermodynamically probable but it does not occur under ordinary conditions. Why?

26. Figure 32 shows the phase diagram of the SO_3-H_2O system.

(a) What compounds are found in this system?

(b) What is oleum?

(c) How shall concentrated sulphuric acid be mixed with water?

Experiment 27. Dehydrating Properties of Concentrated Sulphuric Acid. Place concentrated sulphuric acid into a test tube and immerse a flint into the acid for a while. Observe and explain.

27. Compare the structures of the H_2SO_4, H_2SO_3S and $H_2SO_3(O_2)$. What effect will a substitution of the oxygen atom in the tetrahedral ion SO_4^{2-} for the sulphur atom or a peroxy group have on the stability of the compound?

Experiment 28. Obtaining thiosulphuric acid and its decomposition. Examine the action of hydrochloric acid on solution of sodium thiosulphate(VI). Explain the appearance of the precipitate.

28. What oxidation states can be assigned to the sulphur atoms in the thiosulphate ion? What properties, oxidizing or reducing, prevail in thiosulphates?

Experiment 29. Reducing properties of thiosulphates. Add chlorine water by drops to sodium thiosulphate solution. Note the disappearance of chlorine odour and the appearance of the sulphate(VI) ion in the solution.

29. Draw the structural formulas and name the compounds in the following series:

H_2SO_4-$H_2S_2O_7$-$H_2S_3O_{10}$; $H_2S_2O_6$-$H_2S_3O_6$-$H_2S_4O_6$; H_2SO_4-H_2SO_5-$H_2S_2O_8$

How will the stability of the chain $-\overset{|}{\underset{|}{S}}-\overset{|}{\underset{|}{X}}-\overset{|}{\underset{|}{S}}-$ change if the oxygen atom in the bridge (X) is substituted for the peroxy or persulpho group?

Experiment 30. Obtaining sodium tetrathionate and its properties. Add, by drops, sodium thiosulphate solution into a test tube filled with iodine water until the solution discolours. Add dilute sulphuric acid to the solution and see if any appreciable change takes place.

Experiment 31. Formation and decomposition of persulphuric acid. Add dilute sulphuric acid to solution of ammonium persulphate. Describe the nature of the gas evolved.

Experiment 32. Oxidizing properties of persulphates. (a) Add a solution of ammonium persulphate to potassium iodide solution. Explain the change in the solution colour.

(b) Heat a solution of a chromium(III) salt acidified with sulphuric acid and containing a few drops of $AgNO_3$. Add crystalline ammonium persulphate to the hot solution and heat again until orange colour develops. Write the reaction equation assuming that the $Cr_2O_7^{2-}$ ion is formed and the Ag^+ ion acts as a catalyst.

2.3. The Elements of the Selenium Subgroup

30. Construct graphs showing the variation of the atomic radii, the first ionization energy and the electron affinity with the atomic number for the *p*-elements of group VI. Explain the curves.

31. Compare the structure of crystals of oxygen, sulphur, selenium, tellurium, and polonium.

(a) Construct a graph showing the dependence $T_m = f(Z)$. How does the melting point change in the transition from oxygen to polonium? Explain your answer.

(b) Which of the discussed simple substances are dielectrics and which are semiconductors?

(c) Calculate the exciting wavelength at which the selenium electrons will be moved from the valency zone into the conduction zone ($\Delta E = 1.87$ eV). Explain the increasing conductivity of selenium on exposure to light.

Experiment 33. Selenium semiconductor photo-voltaic cell. Connect, in series, a selenium photo-voltaic cell and a galvanometer. Note the instrument readings during exposure of the cell to light and in the dark.

32. Give examples of reactions which evidence that the chemical nature of simple substances changes in the transition from oxygen to polonium.

(a) How does the oxidizing (nonmetallic) activity change in the transition from oxygen to tellurium and what effect it has on the possibility of formation of H_2E by direct interaction of simple substances? Prove your answer by ΔG_{fH_2E} data of the corresponding reactions. How can hydrogen selenide and hydrogen telluride be obtained?

(b) How does the strength of the E—H bond and the acid strength change in the series H_2O-H_2Te? Explain your answer.

(c) How do the reducing properties change in this series? Compare the values of E° for the corresponding systems to prove your answer.

33. Give examples of binary compounds and the corresponding anion complexes of selenium(IV), tellurium(IV) and polonium (IV).

(a) Describe the structure of these binary compounds in the gaseous state.

(b) Give examples of the reactions illustrating the acid-base properties of EO_2 and $EHal_4$.

34. Calculate the heat of sublimation of SO_2, SeO_2 and TeO_2. Describe the structure of the dioxides in the solid state and explain the character of variation of heat of sublimation and the melting point in the series SO_2—SeO_2—TeO_2.

35. What reactions will occur on mixing together: (1) acidified solutions of oxysulphate(IV) and oxyselenate(IV); (2) solutions of selenious acid and acidified solution of $KMnO_4$?

Experiment 34. Comparing the oxidation-reduction properties of SeO_3^{2-} and SO_3^{2-}. Obtaining selenium. (Use the hood!) Add saturated solution of sodium sulphite to a concentrated solution of H_2SeO_3, or a selenite solution acidified with hydrochloric acid, and heat: a red-brown amorphous substance precipitates. Explain.

Experiment 35. Oxidation and reduction properties of selenium (IV) and tellurium (IV) compounds. (a) Add $SnCl_2$ and Na_2SO_3 solutions, respectively, to H_2SeO_3 and $TeCl_4$ solutions acidified with HCl. Explain your observations.

(b) Add, by drops, $KMnO_4$ solution to H_2SeO_3 and TeO_2 solutions acidified with nitric acid. Explain your observations.

36. Describe the structure of SeO_3, TeO_3, EF_6 and the corresponding anion complexes.

CHAPTER 3

p-Elements of Group V

3.1. Nitrogen

1. Construct the energy diagram of the orbitals and give electron configurations for the ground states of the nitrogen molecule and molecular N_2^+ and N_2^- ions.

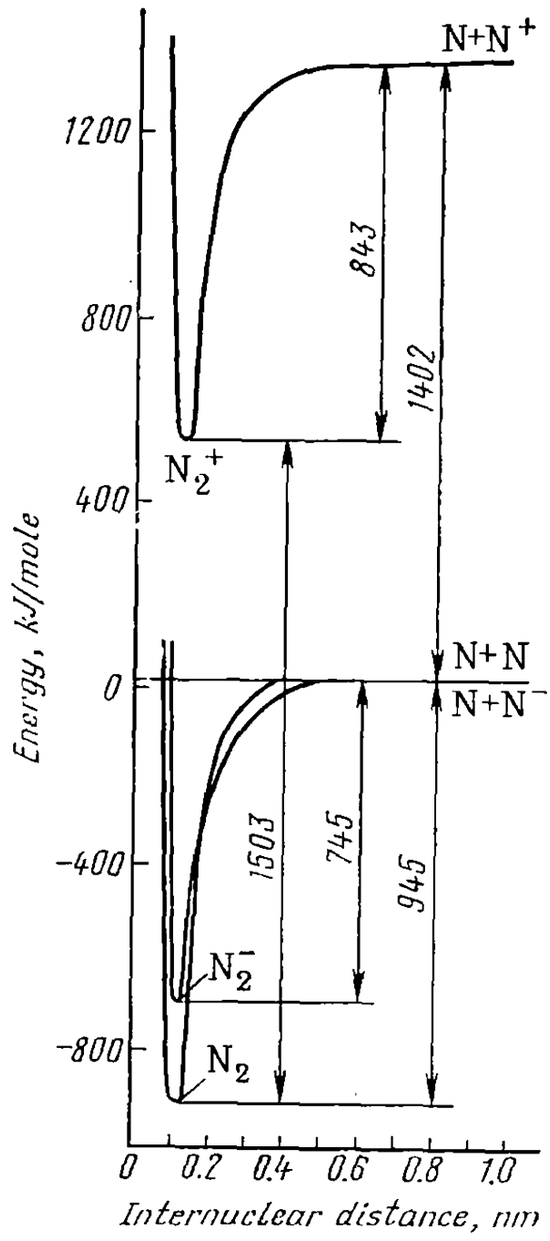


Fig. 33. Variation of potential energy of the molecules and ions N_2, N_2^+ and N_2^- with the internuclear distance

(a) What are the dissociation energy and the internuclear distance in the series N_2^+-N_2-N_2^-? How do they vary in the series (Fig. 33)?

(b) Compare the values of the ionization energy and of the electron affinity of the nitrogen atom and the nitrogen molecule. How do they vary in the transition from the atom to the molecule of nitrogen?

(c) Explain the chemical inertness of molecular nitrogen. How can it be rendered active?

2. Spectrally pure nitrogen can be prepared by the thermal decomposition of sodium azide. Less pure nitrogen can be obtained by thermal decomposition of ammonium nitrite.

(a) Calculate ΔH°_{298} and ΔS°_{298} of the processes.

(b) What type—reversible or irreversible—are these processes?

Experiment 1. Preparing nitrogen by decomposition of ammonium oxynitrate (III). Place equal volumes of saturated solutions of sodium oxynitrate (III) and ammonium chloride into a test tube (not more than one third) and heat slightly until the reaction begins. Explain your observations.

3. Give ΔH°_f and ΔS°_f of oxides of nitrogen. Construct the graph for $\Delta G^\circ_f = f(T)$.

(a) What oxide and why can be formed by direct oxidation of nitrogen with oxygen?

(b) What conditions are required to oxidize nitrogen by oxygen?

4. Give examples of basic, acid and amphoteric nitrides.

(a) How do they react with water?

(b) Nitrides of what elements are known for their refractoriness and chemical stability? What is the purpose of metal and alloy nitration? Describe the main principle of the nitration reaction.

Experiment 2. Formation of magnesium nitride. (Oxidizing properties of nitrogen.) Close a crucible containing magnesium chips with an asbestos sheet and heat for one-two hours over a slight flame: magnesium oxide forms in the upper part of the crucible and green magnesium nitride in the lower part of the crucible. Add water, by drops, to the nitride obtained. Identify the evolving gas.

5. Calculate ΔH°_{298}, the ΔS°_{298} and ΔG°_{298} of the reaction of ammonia synthesis.

(a) How do ΔG, the equilibrium state and the rate of synthesis depend on temperature?

(b) Substantiate the choice of conditions for industrial synthesis of ammonia (see Fig. 15).

(c) Write the equations of the reactions used for preparing ammonia in the laboratory.

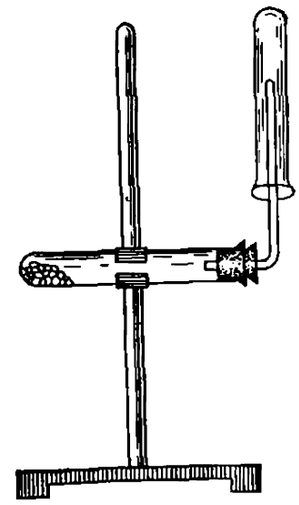


Fig. 34. Obtaining ammonia

Experiment 3. Preparing ammonia from ammonium salts and its solubility in water. (Use the hood!) Mix thoroughly equal volumes of ammonium chloride and calcium hydroxide, transfer the mixture into a dry test tube, close it with a stopper provided with a gas oultet tube and fix the test tube in a stand in position shown in Fig. 34. Put a dry test tube on the gas outlet tube to collect ammonia. Heat the mixture gently, moving the burner along the test tube. When the test tube is filled with ammonia, remove it carefully from the gas outlet tube and (without turning over) stopper it.

Dissolve NH_3 in water. To do it, immerse the test tube containing ammonia (its mouth down) into water in a dish and remove the stopper. Examine the medium of the obtained solution. Explain your observations.

6. It has been proved experimentally that the first ionization potential of NH_3 molecule has three values: 10.5 eV, 15.2 eV and 22.4 eV. Explain it by the theory of molecular orbitals.

7. Describe the structure of the NH_3 molecule. Explain its high polarity, marked tendency to the donor-acceptor interaction, ready liquefaction and high heat of vaporization, high solubility in water and alkalinity of aqueous solution.

Experiment 4. Shifting of ionic equilibrium of aqueous ammonia. (Use the hood!) Determine the reaction of a dilute solution of ammonia in water. Explain the intensified smell of ammonia when the solution is heated or acted upon with alkali. Explain also the change of the indicator colour when hydrochloric acid is added.

Experiment 5. Formation of ammonium salts. (Use the hood!) Wet the bottom and the walls of a beaker with concentrated hydro-

chloric acid and discard excess acid. Cover a crucible containing ammonia solution with the beaker. Explain your observations.

Experiment 6. Hydrolysis of ammonium salts. Determine the reaction of the medium of NH_4Cl and $(NH_4)_2SO_4$ solutions. Why does solid $(NH_4)_2CO_3$ smell of ammonia?

8. (a) Calculate ΔH°_{298}, ΔS°_{298}, ΔG°_{298} and ΔG°_{573} of the thermal decomposition of crystal ammonium oxynitrate (V) with the formation of: (1) ammonia; (2) nitrogen(I) oxide.

(b) How does the probability of these reactions depend on temperature? Which of them is practically irreversible?

(c) Write equations of thermal decomposition of NH_4Cl, $(NH_4)_2CO_3$, $NH_4H_2PO_4$ and $(NH_4)_2Cr_2O_7$. Compare them with the equations of decomposition of NH_4NO_2 and NH_4NO_3. Which of these reactions is reversible and which is practically irreversible?

(d) How does the character of thermal decomposition of ammonium salts depend on the nature of the anion?

Experiment 7. Action of heat on ammonium salts. (Use the hood!) (a) Fix a test tube containing ammonium chloride in a stand and heat. A white deposit appears on the test-tube walls. Explain.

(b) Heat a dry test tube containing ammonium dihydrophosphate. Identify the evolving gas.

(c) Try similarly the action of heat on ammonium carbonate crystals. Explain the absence of sublimation.

(d) Fix a test tube containing ammonium dichromate vertically in a stand and heat until the reaction begins. Explain the volcanic character of the reaction. Keep the solid product of the decomposition.

9. Explain the difference between the frequency of valency oscillations of the N—H bond of ammoniates and the free ammonia molecule:

	H_3N	$[Co(NH_3)_6]^{3+}$	$[Cr(NH_3)_6]^{3+}$	$[Ni(NH_3)_6]^{2+}$
$\tilde{\nu}_{NH}$, cm^{-1} . . .	3414	3320	3320	3397

Experiment 8. Obtaining nickelous ammoniate. Add excess ammonia water to a nickelous sulphate solution. Explain your observations.

10. Write the equation of the autoionization of liquid ammonia.

(a) What compounds in liquid ammonia act as acids and bases?

(b) Write examples of the reactions in liquid ammonia: neutralization; interaction of basic nitride with ammono acid; reaction of acid nitride and ammono base; interaction between liquid ammonia and chlorine.

Experiment 9. Obtaining liquid ammonia and dissolving sodium in it. (Use the hood!) The apparatus for this experiment is shown in Fig. 35. Separate gaseous ammonia, obtained by heating ammonia water in a flask *1* (or from a cylinder), from water vapour in a reflux condenser *2* and in an absorber *3* packed with CaO. Condense dry am-

monia in a test tube *4* cooled with liquid nitrogen (do not use liquid air or oxygen) in a Dewar flask *5*. If the test tube reaches the surface of liquid nitrogen, ammonia freezes into white crystals which melt when the test tube is raised above the surface of liquid ammonia. When about 1 ml of liquid ammonia is condensed, stop ammonia flow.

Place a piece of sodium metal (about 0.1 g) into liquid ammonia: a bright coloured solution of sodium in liquid ammonia is formed. Raise slowly the test tube above the surface of liquid nitrogen: ammonia evaporates and sodium precipitates as a lustrous deposit on the test-tube walls. When the experiment is over, keep the test tube with sodium in air and then wash with water.

11. The proton affinity of the ammonia molecule is 9.3 eV, and of water, 7.9 eV. Aqueous solutions of acetic and perchloric acids are markedly different with respect to their strength. The solutions of these acids in liquid ammonia are fully ionized. Why is the different strength of the acids in aqueous solution levelled in liquid ammonia?

12. Calculate ΔG°_{298} of oxidation of ammonia by oxygen with the formation of nitrogen(II) oxide and molecular nitrogen.

(a) Which of these processes is more likely to occur in burning ammonia?

(b) How is oxidation of H_3N controlled in industry to obtain predominantly NO?

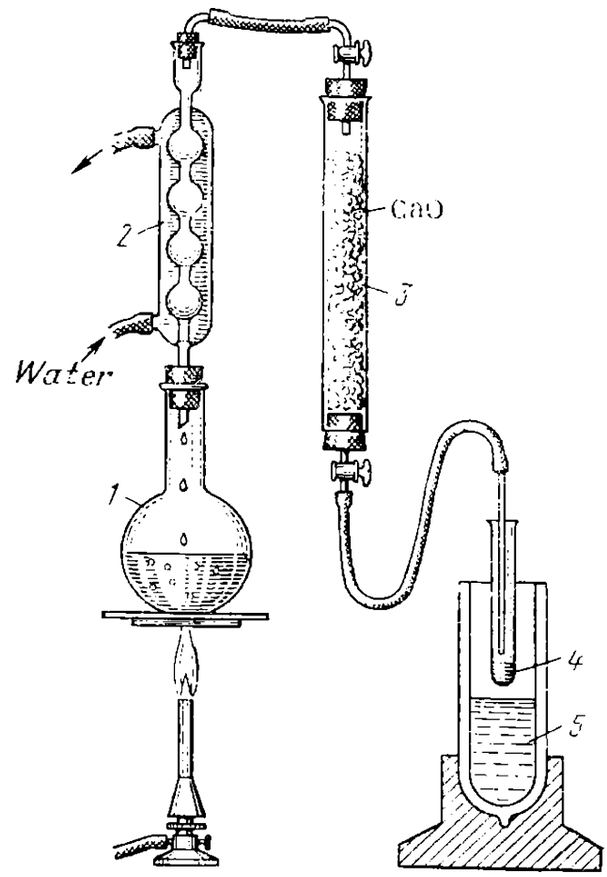


Fig. 35. Apparatus for obtaining liquid ammonia

Experiment 10. Burning of ammonia in oxygen. (Use the hood!) Use apparatus shown in Fig. 36 to observe the process of ammonia burning in oxygen. Heat carefully the flask *1* containing 40-50 ml of concentrated ammonia solution (if the solution boils, move the burner aside). Let oxygen pass slowly from a cylinder into the vessel *2* and light the gas mixture at the outlet of tube *3*. Ammonia burns with a yellowish-green flame. If the flame is torn off, decrease the oxygen flow.

Experiment 11. Oxidation of ammonia in the presence of a catalyst. (Use the hood!) Wet a 2-3-litre flat-bottomed flask with concentrated ammonia solution. Stopper the flask. Take chromic oxide by a spoon and calcine it in the flame of a burner. Insert quickly the spoon

into the flask neck and unload it with shaking. Explain your observations. Repeat the experiment using a hot platinum net as a catalyst.

13. Once the structure of the hydroxylamine is known, characterize its donating and accepting properties, molecular association, autoionization, reaction with water and acids, and oxidation-reduction properties. Give examples of reactions.

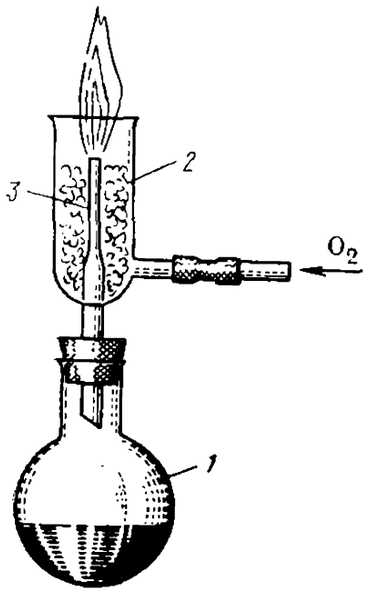


Fig. 36. Apparatus for combustion of ammonia

Experiment 12. Oxidizing and reducing properties of hydroxylamine. Add, by drops, hydroxylammonium sulphate solution or hydroxylamine sulphate to acidified solutions of $KMnO_4$ and $FeSO_4$: the colour of the solution changes. Explain.

14. Describe the structure of the molecules of chlorine nitride and nitrogen (III) fluoride.

(a) What is the most probable hybridization of the nitrogen atom orbitals in these molecules?

(b) What are the products of the hydrolysis of Cl_3N and NF_3?

15. Single and multiple bonds of nitrogen and carbon are characterized by the following energy and length:

	$-\ddot{N}=\ddot{N}-$	$-\overset{\cdot\cdot}{\underset{\vert}{N}}-\overset{\cdot\cdot}{\underset{\vert}{N}}-$	$-\overset{\vert}{C}=\overset{\vert}{C}-$	$-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$
E, kJ/mole . .	418	155	606	334
d, nm	0.125	0.146	0.135	0.155

(a) Explain the great difference in stabilities of the homochains of nitrogen and carbon.

(b) Give examples of compounds with bonds —N=N— and —N—N—. Characterize their stability.

16. Here are some constants of hydrazine: m. p., 2°C, b. p., 114°C, $\mu = 1.85$ C·m, $\Delta H^{\circ}_{comb} = -622$ kJ/mole.

(a) Describe the structure of the hydrazine molecule and explain its state of aggregation, autoionization in the liquid state, ability to form hydrazonium salts, oxidation-reduction properties.

(b) Can hydrazine be synthesized from simple substances? Give equations of reactions by which hydrazine is obtained.

(c) Calculate the heat effect of combustion of 1 kg of hydrazine.

(d) What properties are responsible for the use of hydrazine as rocket fuel?

Experiment 13. Reducing properties of hydrazine. Add, by drops, hydrazonium sulphate solution to potassium oxymanganate(VII)

solution acidified with dilute solution of sulphuric acid. Explain your observations.

17. Distribute electrons in the orbitals of the NO molecule and NO^+ molecular ion. Give the values of the internuclear distance and dissociation energy of NO and NO^+.

(a) Explain the different internuclear distance, the dissociation energies and the frequencies of valency oscillations of NO molecule and NO^+ ion ($\tilde{\nu}_{NO} = 1909$ cm^{-1}; $\tilde{\nu}_{NO^+} = 2277$ cm^{-1}).

(b) What tendency (donating or accepting an electron) is more characteristic of the NO molecule? Why?

(c) The products formed in the reactions

$$2NO + Cl_2 = 2NOCl;$$

$$6NO + 8BrF_3 = 6NO[BrF_4] + Br_2$$

are characterized by the following properties: NOCl is gas (m. p. —62°C, b.p. —7°C), $\tilde{\nu}_{NO} = 1800$ cm^{-1}; $NO[BrF_4]$ is crystalline compound (m.p., 255°C), it is a conductor in the liquid state, $\tilde{\nu}_{NO} = 2300$ cm^{-1}.

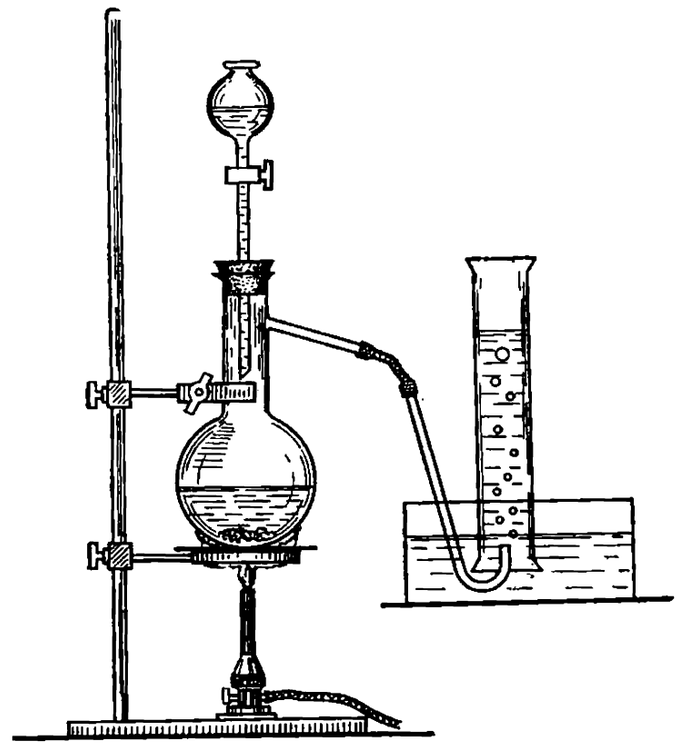


Fig. 37. Apparatus for obtaining nitrogen(II) oxide

In which of these compounds is the NO group bonded by the covalent bond and in which is it in the form of the NO^+ ion?

18. Calculate the heat of formation of NO by the dissociation energies of N_2, O_2 and NO.

(a) Why is NO an endothermic compound?

(b) Why do phosphorus, carbon and sulphur continue burning energetically in NO? Calculate ΔG of the corresponding reactions.

(c) Write the equations of the reactions and specify the conditions for production of NO in industry and laboratory.

Experiment 14. Obtaining nitrogen (II) oxide and burning of sulphur and coal in it. (Use the hood!) Place copper chips into a Würtz flask (Fig. 37) and add dilute nitric acid (density, 1.32) from a dropping funnel. Collect nitrogen oxide in cylinders by displacing water from them. Ignite sulphur (coal) and let fire catch it well. Introduce the burning material into the cylinder filled with nitrogen (II) oxide.

19. (a) Describe the structure of a fluoride, oxyhalide, nitrogen (III) oxide and explain their states of aggregation in normal conditions.

(b) Give examples of reactions to illustrate the acid-base properties of these compounds.

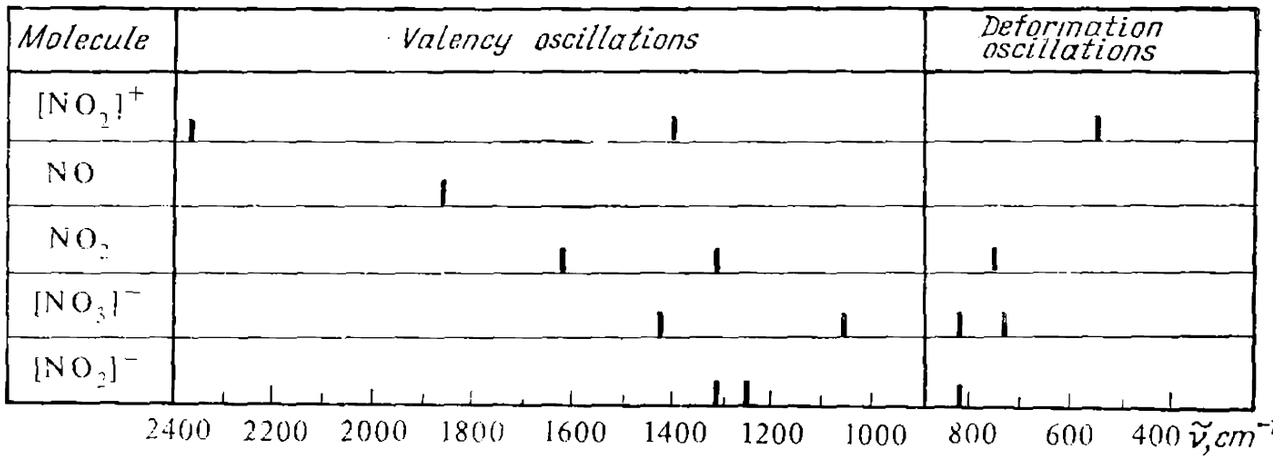
20. Give examples of reactions to illustrate the oxidizing and reducing properties, and also examples of disproportionation of the NO_2^- ion.

Experiment 15. Oxidation-reduction properties of the oxynitrate (III) ion. Try the action of sodium (potassium) nitrite solution on acidified solutions of potassium iodide and potassium oxymanganate (VII).

Experiment 16. Disproportionation of the oxynitrate (III) ion (formation and decomposition of HNO_2). (Use the hood!) Heat sodium nitrite crystals in a test tube containing concentrated sulphuric acid. Explain the appearance of a red-brown vapour.

21. The NO_2 molecule is characterized by the following constant: $\mu = 0.29$ C·m, $\angle$ ONO = 132°, $d_{NO} = 0.120$ nm, $E_{NO} = 468.8$ kJ/mole.

(a) What is the spatial configuration of the NO_2 molecule? There are three absorption bands in the I-R spectrum of the NO_2 molecule and only one in the NO molecule. Why?



(b) Can NO_2 be formed from simple substances? Write the equations of the reactions for the production of NO_2 in industry and in laboratory.

(c) Why do many metals and nonmetals burn in NO_2?

22. After absorption of NO_2 in an alkali solution, the products were obtained whose I-R spectra are shown in Fig. 38.

(a) Using the data given in Problem 21 identify the spectra.

(b) Write the equation of the reaction of NO_2 with hydroxides of alkali metals. What is the industrial use of this reaction?

Experiment 17. Formation and disproportionation of NO_2. (Use the hood!) Place anhydrous lead(II) oxynitrate(V) in a refractory test tube, close it tightly with a stopper through which an outlet tube is passed, fasten the test tube in the stand and heat carefully.

Try the action of the evolving gas on water and alkali solution. To that end, pass NO_2 into a test tube half-filled with cold water.

Determine the pH of the solution obtained. Use part of the solution to reveal the NO_2^- ion (using a very dilute solution of $KMnO_4$ or KI). Boil the remaining solution well. Check to see that the acid properties of the solution persisted. Test it for the presence of the NO_2^- ion. Explain your observations.

Pass NO_2 through an alkali solution for 2 minutes. Acidify the obtained solution with dilute sulphuric acid and examine it for the presence of the NO_2^- ion (using the solution of KI or $KMnO_4$).

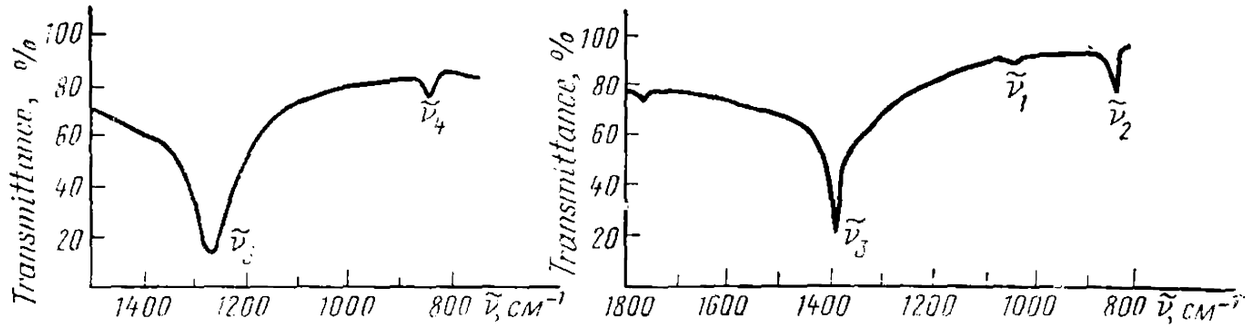


Fig. 38. Infra-red spectra of nitrogen compounds

23. Autoionization of liquid N_2O_4 occurs as follows: $N_2O_4 \rightleftarrows NO^+ + NO_3^-$. N_2O_4 can therefore be used as an ionizing solvent to obtain anhydrous oxynitrates(V) of metals.

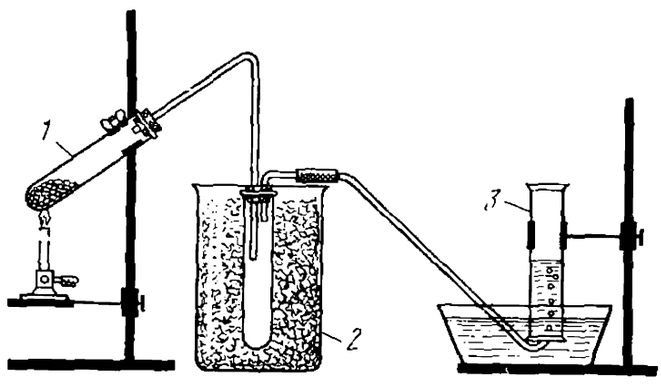


Fig. 39. Apparatus for obtaining liquid N_2O_4

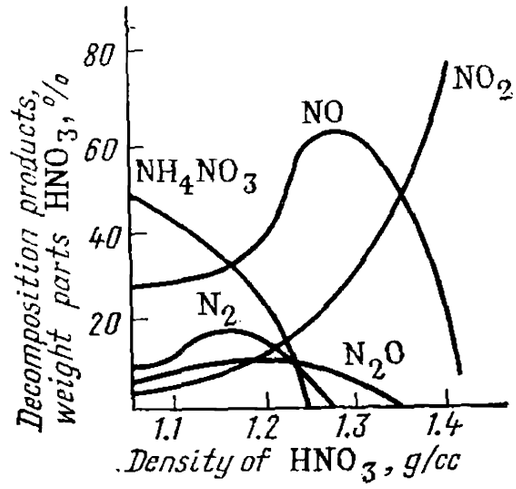


Fig. 40. Effect of concentration of nitric acid on the character of products of its reduction by iron

(a) Write the equation of the reaction of zinc with liquid N_2O_4.

(b) What are the properties (acid or basic) of NOCl and $AgNO_3$ in liquid N_2O_4? Write the equation of the reaction between NOCl and $AgNO_3$ dissolved in liquid N_2O_4.

(c) How can liquid N_2O_4 be obtained?

Experiment 18. Preparing liquid N_2O_4. (Use the hood!) Assemble the apparatus as shown in Fig. 39. Close tightly a refractory test

tube *1* containing lead oxynitrate(V) with a stopper through which a gas outlet tube is passed and heat. The products of thermal decomposition are yellow lead oxide which remains in the test tube *1*, nitrogen dioxide which is condensed in the beaker *2* cooled in a mixture of snow and salt, and oxygen which is collected in the cylinder *3* filled with water.

Experiment 19. Burning of metals and nonmetals in nitrogen dioxide. (Use the hood!) Collect nitrogen dioxide into two thick-wall glass cylinders. Heat magnesium (copper, zinc) to 200-300°C and put it into the cylinder. Light up sulphur (phosphorus, coal) and put into the cylinder as well. Explain your observations.

24. The study of the I-R spectra of solid nitrogen(V) oxide has revealed the following oscillation frequencies: 1400, 538, 2375 cm^- and 1050, 824, 1413 and 722 cm^{-1}. To what ions do these frequencies correspond (see the diagram above)? What structure units compose the crystals of N_2O_5?

25. Anhydrous oxynitrates(V) form the following series when arranged in the order of their decreasing thermal stability: nitrates of the alkali metals (575-675°C); nitrates of the alkaline-earth metals (575-560°C); nitrates of cobalt(II), nickel(II), copper(II), zinc(II) (270-350°C); beryllium (125°C); chromium(III) (50°C); hydrogen nitrate (in normal conditions on exposure to light); halogen (I) nitrates (— 10°C).

(a) Explain the decreasing thermal stability in the series.

(b) Write equations for the reactions of thermal decomposition of $NaNO_3$, $Pb(NO_3)_2$, HNO_3 and $ClNO_3$.

(c) What metal nitrates can be used to obtain NO_2?

Experiment 20. Thermal decomposition of sodium nitrate(V). (Use the hood!) Fix a dry test tube in the vertical position in a stand, place a dish with sand underneath, and add a small quantity of sodium nitrate (saltpetre) into the test tube. Heat the test tube. Add a red-hot piece of coal into the molten saltpetre. When the coal stops burning, add a lump of sulphur. The sulphur catches fire and burns to the end. (Sometimes, the test tube melts due to large amounts of heat evolved in the reaction.) Explain your observations.

Experiment 21. Thermal and photochemical decomposition of hydrogen nitrate. Compare the colour of dilute and fuming nitric acid. Explain the colour of fuming acid and the intensification of the colour on gentle heating.

26. Figure 40 shows the effect of concentration of HNO_3 on the character of products of its reduction by iron.

(a) What are the most probable products of reduction of nitric acid, if iron reacts with the acid of the following densities: (1) 1.1; (2) 1.3; (3) 1.4?

(b) How does the character of the products of their interaction depend on the activity of the reductant and the concentration of the acid? Write the equation for the reactions of zinc and copper with dilute and concentrated nitric acid.

(c) Write equations of reactions of sulphur and phosphorus with concentrated nitric acid. What is the difference in the attitude of metals and nonmetals to nitric acid?

Experiment 22. Oxidizing properties of nitric acid. (Use the hood!) (a) Add dilute (2*N*) solution of nitric acid into a test tube containing copper and magnesium chips. Heat slightly the test tube containing copper. Prove experimentally the formation of ammonium nitrate in the test tube containing magnesium.

(b) Pour 3-4 drops of concentrated nitric acid into a test tube and add three volumes of concentrated hydrochloric acid. Heat the mixture slightly. Put a sheet of filter paper wetted with potassium iodide solution to the mouth of the test tube. Explain your observations.

27. The internuclear distances of the NN_2^- ion are equal to (0.115 nm), while in the HNN_2 molecule the N—N internuclear distances are 0.113 and 0.124 nm.

(a) Explain the differences in bond lengths.

(b) Why is thermal stability of ionic azides higher than that of covalent ones?

3.2. Phosphorus

28. Give values of the atomic radius, the ionization energy and electron affinity of phosphorus and nitrogen.

(a) Explain the differences in said constants.

(b) Explain the differences in the chemistry of phosphorus and nitrogen.

29. Show possible spatial combinations of phosphorus atoms and describe the structure of the main polymorphic modifications of phosphorus.

(a) Under what conditions does white phosphorus convert into red and black phosphorus; and red phosphorus into its white allotrope.

(b) Compare and explain the differences between densities, melting and spontaneous ignition points, solubilities of white, red and black phosphorus in hydrogen sulphide?

Experiment 23. Comparing melting and ignition points of white and red phosphorus.* (Use the hood!). Place a piece of dry white phosphorus on one end of a copper plate and a small amount of red phosphorus on its other end. Place the plate on a tripod and heat over the flame of a burner, nearer to the red phosphorus end. Explain your observations.

Experiment 24. Conversion of red phosphorus into its white form. (Use the hood!) Close a test tube containing a grain of red phosphorus with a cotton pad and heat carefully over a small flame so that the phosphorus should slowly vaporize. Explain the formation of drops of white phosphorus on the walls of the test tube.

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* Remember that white phosphorus and its vapour are highly poisonous. When gets on the skin, white phosphorus causes heavy burns.

30. Write the equations of reactions used to obtain $P_4(g)$ by reduction of $Ca_3(PO_4)_2(c)$ with carbon, with and without the participation of $SiO_2(c)$ in the reaction and with the formation of CO (g) and also of $CaO(c)$ or $CaSiO_3$ (c) respectively.

(a) Decide whether or not the processes will occur at 25°C and 1500°C if they are characterized by the following data (with reference to 1 mole of P_4): (1) without participation of SiO_2: $\Delta H^\circ_{298} = 3388$ kJ, $\Delta S^\circ_{298} = 1955$ J/deg; (2) with participation of SiO_2: $\Delta H^\circ_{298} = 2815$ kJ, $\Delta S^\circ_{298} = 1952$ J/deg;

(b) How does the direction of the reactions depend on temperature? Explain.

(c) How does the oxidation-reduction process depend on the presence of SiO_2? Explain.

31. Give examples of reactions of oxidation, reduction and disproportionation of phosphorus.

Experiment 25. Oxidation of phosphorus by oxygen. (Use the hood!) Light up red phosphorus in a porcelain dish placed on a tripod. Cover the dish loosely with a glass funnel. When the experiment is over, place the funnel in the stand and put a test tube under the funnel. Keep the product of the experiment for further experiments.

32. Describe the structure of the phosphine molecule.

(a) Give values and explain the difference in the bond lengths and energies of bonding, the bond angles and the dipole moments of the ammonia and phosphine molecules.

(b) Compare the stabilities, electron donating and reducing properties, the melting and boiling points of phosphine and ammonia from the point of view of their molecular structure.

(c) Can phosphine be formed from simple substances? Give equations of the reactions for obtaining phosphine.

(d) Explain why the electron affinity of H_3P molecule (8.0 eV) is lower than that of H_3N molecule (9.0 eV)? How does it affect the properties of phosphine and phosphonium derivatives as compared with the properties of ammonium and ammonia?

Experiment 26. Obtaining phosphine by disproportionation of phosphorus. (Use the hood!) Fill 3/4-full of a round-bottom flask with 30-50 per cent KOH solution and drop a piece of white phosphorus, the size of a pea, in it. Close the flask with a rubber stopper through which a gas outlet tube is passed. Lower the free end of the outlet tube into a crystallizer. Heat the flask carefully. Observe the evolution of phosphine, which catches fire spontaneously above the solution.

Experiment 27. Comparing properties of phosphine and ammonia. Assemble the apparatus as shown in Fig. 41. Pour dilute hydrochloric acid into a three-neck bottle *1* and concentrated hydrochloric acid into bottle *2*. Displace air from the apparatus by carbon dioxide. Close clamp *3* and drop calcium phosphide into the bottle through tube *4*.

(a) When phosphine starts evolving, lower the outlet tube into a

test tube containing $NiSO_4$ solution. Explain the different action of H_3P and H_3N (see Experiment 8) on the $NiSO_4$ solution.

(b) Pass phosphine into water. Check to see if the solution reacts alkaline. Compare your observations with the process of ammonia dissolution in water.

33. Describe the structure of $PHal_3$, P_4O_6 and the PO_3H^{2-}.

(a) Give the coordination number and the characteristic unit cell of phosphorus(III) compounds.

(b) Give examples of reactions illustrating the acid-base properties of binary phosphorus(III) compounds.

(c) Explain the formation of the $PCl_3 \cdot BCl_3$ molecule.

34. The bond angles of the following ions are: ClO_3^-—86°, SO_3^{2-}—98°, PO_3^{3-}—103°.

(a) Describe the structure of the ions. How does their electron donating ability vary in the series? Can the PO_3^{3-} ion exist in an aqueous solution?

(b) How does the reducing activity (the ability to convert into the EO_4^{n-} ion) vary in the series ClO_3^-—SO_3^{2-}—PO_3^{3-}?

Experiment 28. Hydrolysis of PCl_3 and reducing properties of PO_3H^{2-}. (Use the hood!) Add, carefully, by drops PCl_3 into a test tube containing water. Divide the contents of the test tube into two parts. Add indicator to one test tube and determine the medium of its contents. Add $AgNO_3$ solution to the other: black silver precipitates. Explain.

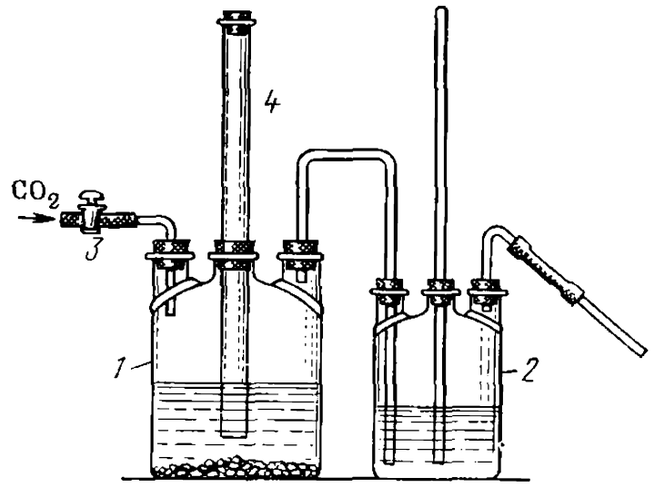

Fig. 41. Apparatus for obtaining phosphine

35. The PO_4 tetrahedron has been proved experimentally to be the unit cell of phosphorus(V) oxycompounds.

(a) How can the PO_4 tetrahedra be combined with one another into another dimer, a chain, a layer?

(b) Describe the structure of the P_4O_{10} molecule (d_{PO} = 0.162 and 0.139 nm) and of one layer of the laminated modification of P_2O_5.

(c) How do the properties of P_2O_5 modifications depend on their structure? Show schematically the hydration of P_4O_{10}.

(d) What acids are present in the system P_2O_5-H_2O at high concentration of P_2O_5? Describe their structure and name them.

Experiment 29. Hydration of phosphorus anhydride and polyphosphoric acids. The formation of silver salts in neutral medium can be used for qualitative detecting of oxyphosphate(V) ion: Ag_3PO_4 is yellow, $AgPO_3$ and $Ag_4P_2O_7$ are white.

Explain the change in the appearance of phosphorus(V) oxide ob-

tained in Experiment 25 on exposure to air. Wash the resultant mass into a test tube and divide the solution into two parts. Add ammonia water to neutralize the solution in the first test tube and prove experimentally that the solution contains the metaphosphate ion. Add distilled water and a few drops of concentrated nitric acid to the solution in the other test tube. Boil the resultant solution several times. Neutralize the solution with ammonia water and prove that the solution contains the orthophosphate(V) ion.

36. Give ionization constants of phosphoric, phosphorous and hypophosphorous acids.

(a) How do these data agree with the structure of the acids?

(b) Which of the acids, H_3PO_3 or H_3PO_2, has a higher reducing activity? Prove your answer by the values of E°_{298} of the corresponding half reactions.

37. Give examples of halides and oxyhalides of phosphorus(V).

(a) Describe their structure.

(b) Illustrate their acid-base properties by the appropriate reactions.

Experiment 30. Hydrolysis of phosphorus pentachloride. (Use the hood!) Determine the products of PCl_5 hydrolysis.

3.3. Elements of the Arsenic Subgroup

38. Construct a graph showing variation of the atomic radius and the first ionization potential of the *p*-elements of group V with the atomic number. Explain the curves.

39. Describe the structure of metallic and nonmetallic modifications of nitrogen, phosphorus, arsenic, antimony, and bismuth.

(a) How do internuclear distances of stable modifications change in the series P-As-Sb-Bi? How do they agree with the increasing metallic character?

(b) How do the melting points of the stable modifications change in the series As-Sb-Bi? Explain.

40. (a) Explain the experimental data shown in Fig. 42.

(b) Why is bismuth used to obtain low-melting alloys? Exemplify your answer and give the structure of the alloys.

Experiment 31. Preparing Wood's metal. Take the metal samples in quantities sufficient to prepare 5 g of the alloy containing 50 per cent of Bi, 25 per cent of Pb, 12.5 per cent of Sn and 12.5 per cent of Cd. Fuse the ingredients in a porcelain crucible. Pour the melt into boiling water. Explain why the alloy does not harden in hot water.

41. Illustrate variation of the chemical nature of simple substances in the series P-As-Sb-Bi on examples of their reaction with nitric acid.

Experiment 32. Reaction of bismuth with nitric acid. (Use the hood!) Examine the attitude of bismuth to concentrated and dilute nitric acid in the cold and with heating. Use $(NH_4)_2S$ solution to establish in what case the Bi^{3+} ion is formed.

42. Give the length and energy of bonds, bond angles, dipole moments of molecules, boiling and melting points, ΔH_f° and ΔG_f° for

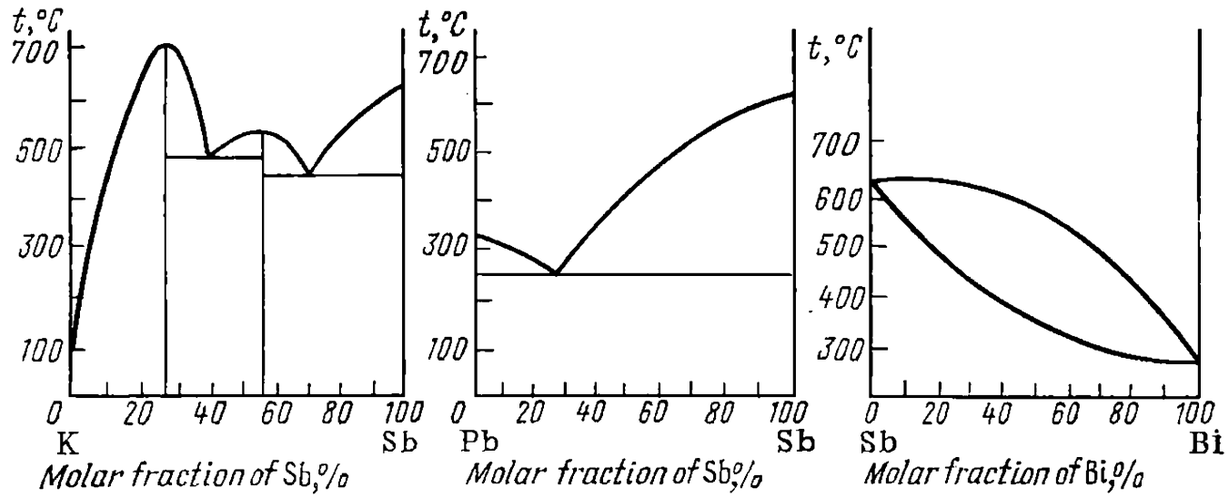

Fig. 42. Phase diagram of the systems K-Sb, Pb-Sb and Sb-Bi

the EH_3 type hydrogen compounds of the *p*-elements of group V.

(a) How do the E—H bond energy and the molecule stability change in the series H_3N-H_3P-H_3As-SbH_3-BiH_3?

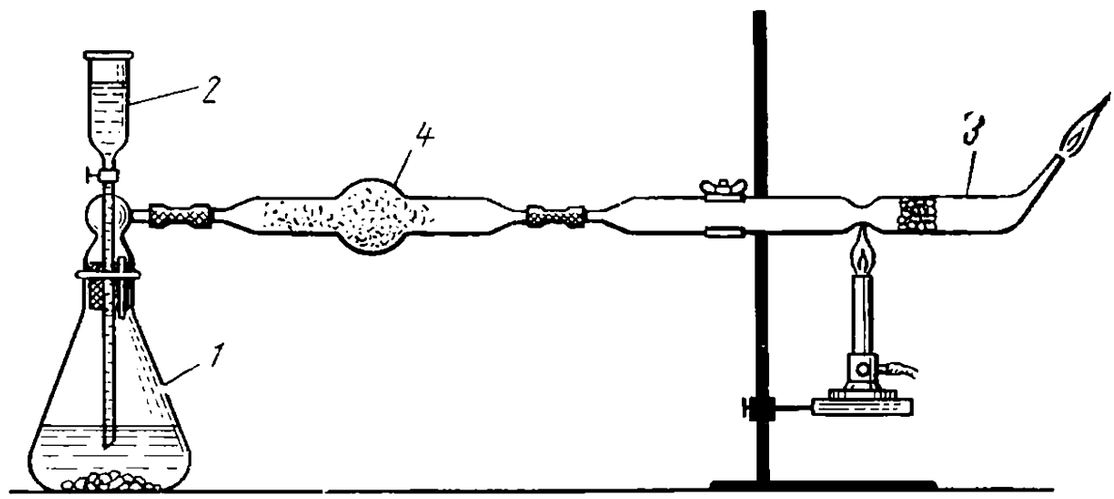

Fig. 43. Apparatus for obtaining arsine

(b) How does the proton affinity change in the series? Explain.

(c) Can AsH_3, SbH_3 and BiH_3 be formed from the simple substances? Describe the methods by which EH_3 can be obtained.

Experiment 33. Obtaining hydrogen arsenide (arsine) (antimonous hydride (stibine)) and its decomposition. (Use the hood!) Figure 43 shows an apparatus used for preparing arsine (stibine) by reducing arsenic compounds with hydrogen. Place 10 g of granulated zinc

into the flask *1*, add (through the funnel *2*) 20 per cent sulphuric acid (60-70 ml) and when the air is all displaced from the apparatus, light the liberated hydrogen at the outlet tube *3*. Add an arsenic (stibic) compound into the flask *1* through the funnel *2* taking special care to prevent air penetration into the apparatus. Explain the appearance of a bluish flame and white fumes in the tube *4*. Heat the narrow part of the tube *3*. Explain the deposition of a black mirror on the cold parts of the tube.

When the experiment is over, fill the flask with water through a dropping funnel and disassemble the apparatus. Treat the deposited arsenic (antimony) with chloride of lime solution.

43. What unit cells are characteristic of compounds of As(III), Sb(III) and Bi(III), if the coordination numbers of E(III) are 3, 4, 5 and 6?

(a) Describe the structure of AsF_3, BiF_3 and Bi_2O_3.

(b) Explain the elevation of the melting point in the series of fluorides and oxides of the *p*-elements of group V. Why does the melting point sharply increase in the transition from SbF_3 to BiF_3 and from As_2O_3 to Sb_2O_3 and Bi_2O_3?

	NF_3	PF_3	AsF_3	SbF_3	BiF_3
Melting point, °C	—206.5	—151	—5.95	292	730
	N_2O_3	P_2O_3	As_2O_3	Sb_2O_3	Bi_2O_3
Melting point, °C	—101	23.8	274	656	820

44. Calculate ΔG°_{298} of hydrolysis of PCl_3 and $AsCl_3$.

(a) In which case is the hydrolysis reversible and in which is it practically irreversible?

(b) Write equations of $SbCl_3$ and $BiCl_3$ hydrolysis.

(c) Explain the variation of the acid-base properties in the series $PHal_3$-$AsHal_3$-$SbHal_3$-$BiHal_3$.

Experiment 34. Hydrolysis of chlorides of antimony(III) and bismuth(III), and its reversibility. Add water to $SbCl_3$ solution. Explain precipitation of an amorphous substance. Add an acid solution. What happens to the precipitate? Hydrolyze $BiCl_3$ following the same instructions.

45. Figure 44 shows the phase diagram of the KCl-$BiCl_3$ system.

(a) What halide complexes are formed by the reaction of halides of As(III), Sb(III) and Bi(III) with basic halides?

(b) Explain the structure of these complexes using the data given in Problem 43.

Experiment 35. Obtaining potassium tetraiodobismuthate(III). (see page 53).

46. Give examples of reactions to illustrate the variation of the acid-base properties of oxides, hydroxides and sulphides of E(III) in the series As(III)-Sb(III)-Bi(III).

Experiment 36. Obtaining hydroxides of antimony(III) and bismuth(III) and comparing their chemical nature. Obtain hydroxides

of Sb(III) and Bi(III) by exchange reactions. Establish which of them is amphoteric under given conditions.

Experiment 37. Obtaining sulphides of arsenic(III), antimony (III) and bismuth(III) and comparing their chemical nature. Obtain sulphides of As(III), Sb(III), and Bi(III). Note their colour. Divide the precipitates into two parts and try them with hydrochloric acid and ammonium sulphide solution. Act with excess hydrochloric acid on solutions of thiosalts. Explain your observations.

47. Give formula of the simplest hydroxides of arsenic(V) and antimony(V) and equations of the reactions by which they are obtained.

48. Molten halides of As(V) and Sb(V) can dissolve various halides to form complexes, for example:

$$AsF_5 + O_2F_2 = O_2[AsF_6] + 1/2F_2;$$
$$SbF_5 + KF = K[SbF_6];$$
$$SbCl_5 + ICl = I[SbCl_6].$$

(a) What properties (acid or basic) of As(V) and Sb(V) halides are demonstrated by these reactions?

(b) Explain the increasing electric conductivity of said systems as compared with melts of arsenic(V) and antimony(V) halides.

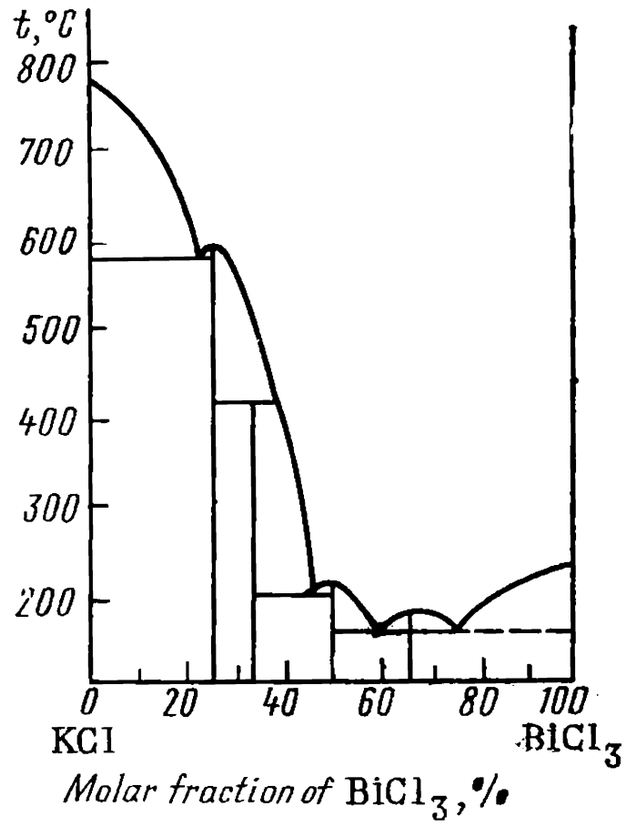

Fig. 44. Phase diagram of the system KCl-$BiCl_3$

49. How does the reducing activity change in the series As(III)-Sb(III)-Bi(III) and the oxidizing activity change in the series As(V)-Sb(V)-Bi(V)? Give values of E° of the corresponding systems to prove your answer.

Experiment 38. Oxidation of antimony(III) and bismuth(III) compounds. (Use the hood!) (a) Add iodine solution to an acidified solution of Sb(III) compound: the colour of the solution vanishes. Explain.

(b) Heat a mixture of 1 ml of $Bi(NO_3)_3$ solution and 3 ml of 30 per cent NaOH solution to boiling. Pass chlorine into the mixture until a dark-brown substance precipitates. Separate the precipitate on a filter, wash it and keep for the next experiment. Explain your observations.

Experiment 39. Oxidizing properties of bismuth(V) compounds. Add 2-3 drops of $MnSO_4$ solution to 3-4 ml of dilute HNO_3. Now add sodium oxybismuthate(V) using a glass rod: crimson colour (the MnO_4^- ion) develops. Explain.

50. Add KI solution to an acidified H_3AsO_4 solution: iodine is liberated. Add solid $NaHCO_3$ to the mixture: the colour of the solution vanishes. Explain your observations.

CHAPTER 4

p-Elements of Group IV

4.1. Carbon

1. From the standpoint of the valency bond theory, indicate what hybrid states of the valency orbitals, the corresponding coordination numbers and unit cells are characteristic of carbon?

2. Figure 45 shows X-ray patterns of diamond (*a*) and graphite (*b*).

(a) Explain the sharp differences in these patterns. Describe the structure of diamond, graphite, carbin and their physical properties.

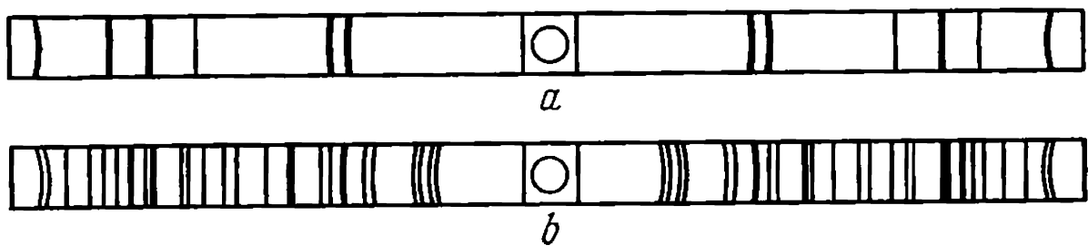

Fig. 45. X-ray patterns of diamond (*a*) and graphite (*b*)

(b) What are the standard entropies of diamond and graphite and how do they relate with the structure of these simple substances?

(c) Explain the different behaviour of diamond and graphite in chemical reactions, for example in the reaction with fluorine.

3. Heats of combustion of diamond, graphite and carbin are —394.1, —396.3, and —356.1 kJ/mole respectively.

What carbon modification is the most stable in normal conditions? Under what conditions do the modifications convert into one another?

4. Figure 46 shows variation of ΔG_f° (kJ/mole O) of some oxides with temperature.

(a) Why does increasing temperature produce different effect on the character of changes in ΔG_f of CO, CO_2 and metal oxides?

(b) Why can carbon reduce almost all metals from their oxides under the appropriate conditions?

(c) What oxide (CO or CO_2) is likely to be formed by burning carbon?

5. It has been established experimentally that a methane molecule can give off one electron, $CH_4 = CH_4^+ + e^-$, the potentials being 13.2 and 22.4 eV. Explain this fact from the point of view of electron distribution in energy levels of the methane molecule.

6. Construct a graph showing the variation of the internuclear dis-

tance d_{CC} with the bond order n_{CC} in C_2H_2 (0.121 nm), C_2H_4 (0.135 nm), C_2H_6 (0.154 nm) and C_6H_6 (0.139 nm). Explain the curves.

(a) The internuclear distance d_{CC} in CaC_2 crystal is 0.129 nm. What type of carbide, methanide or acetylide, is CaC_2?

(b) What are the products of hydrolysis of methanides and of acetylides and what is the industrial use of hydrolysis of CaC_2?

Experiment 1. Hydrolysis of calcium acetylide. (Use the hood!) Place a few drops of water into a test tube containing calcium carbide. Explain your observations.

7. According to experimental data the molecules of $CHal_4$, CO_2 and CS_2 are nonpolar while the molecules of CO, $COHal_2$ and $CSHal_2$ are polar.

(a) Explain this fact from the standpoint of spatial configuration of molecules.

(b) To what type of hybridization of the carbon valency orbitals does the structure of the molecules belong?

8. Construct a graph showing the variation of d_{CHal}, E_{CHal}, ΔS°_{298} and ΔG°_{298} in the series CF_4-CCl_4-CBr_4-CI_4.

(a) Explain the curves.

(b) How do the melting and boiling points change in the series CF_4-CI_4? Explain.

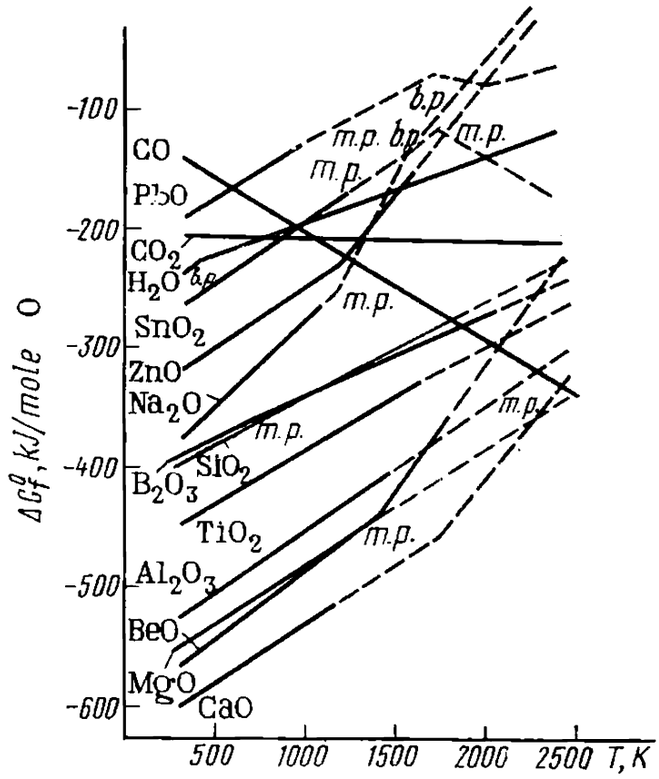

Fig. 46. Variation of ΔG°_f of some oxides with temperature (see the legend for Fig. 21)

9. The values of ΔG°_{298} of hydrolysis of CF_4, CCl_4 and $COCl_2$ are —150 kJ/mole, —251 kJ/mole and —211 kJ/mole. But the hydrolysis of CF_4 and CCl_4 does not occur under normal conditions while $COHal_2$ compounds are readily hydrolyzed. Explain.

Experiment 2. Reaction of carbon tetrachloride with water. Add a few drops of CCl_4 into a test tube containing water and heat the test tube. Test the solution for the presence of the CO_3^{2-} ion.

10. (a) Using Fig. 46 indicate the simple substances (out of those shown in the diagram) that can be oxidized by CO_2.

Why does CO_2 not sustain burning of carbon compounds?

Experiment 3. Carbon dioxide and its properties. (Use the hood!) Fill three dry bottles with carbon dioxide (from a Kipp generator or a cylinder). Check to see if the bottles are filled with carbon dioxide to their full capacity.

(a) Light a magnesium band and place it quickly into a bottle

filled with CO_2. Can a fire extinguisher be used to quench burning magnesium?

(b) Light red phosphorus in a spoon and put it into a bottle filled with CO_2. Explain your observations. Can a fire extinguisher be used to fight burning phosphorus?

(c) Place a small amount of petrol into a porcelain dish and light it. "Pour" CO_2 from the bottle on the burning petrol. Explain your observations.

11. Write structural formulas of trioxy-, trisulphide (trithio-), dinitride, oxynitride, nitride sulphide carbonate ions.

(a) To what type of hybridization of carbon orbitals does the structure of these ions correspond?

(b) Write equations of reactions by which the corresponding carbonates are obtained.

(c) What oxycarbonates and sulphocarbonates are insoluble in water?

Experiment 4. Difference in solubility of oxycarbonates and hydrocarbonates. Pass CO_2 through lime water until the precipitate, which first falls out, is dissolved. Place the solution into two test tubes. Boil one portion, add lime water to the other. Explain your observations.

12. Calculate the temperature of decomposition (p_{CO_2} = = 101.325 kPa) of the following oxycarbonates: Na_2CO_3, $BaCO_3$, $MnCO_3$, $PbCO_3$.

(a) Explain the difference in the temperatures of decomposition of the carbonates.

(b) Explain the instability of H_2CO_3.

(c) What naturally occurring carbonate is used to obtain CO_2 in industry?

Experiment 5. Comparing thermal stability of oxycarbonates. Place $CaCO_3$ and $BaCO_3$ into two test tubes provided with outlet tubes. Lower the outlet tubes in lime water and heat the test tubes. In what case can the CO_3^{2-} ions be detected?

13. According to available data, the hydrogen dinitrocarbonate (cyanamide) molecule has a planar structure: $d_{HN} = 0.094$ nm, $d_{NC} = 0.135$ nm, $d_{CN} = 0.116$ nm, $\angle$ HNH = 120°.

(a) Explain the structure of the H_2CN_2 molecule.

(b) Write the equations of H_2CN_2 hydrolysis and of formation of $CaCN_2$ from CaC_2 and N_2. What oxidation states can the elements in the CN_2^{2-} ion have?

(c) Write the equation of the reaction for which calcium cyanamide is used as nitrogenous and lime fertilizer. How can the products of this reaction be detected?

Experiment 6. Hydrolysis of calcium nitrocarbonate. (Use the hood!) Add a few drops of water to $CaCN_2$ in a test tube and heat until ammonia starts evolving. Explain your observations.

14. What are the oxidation-reduction properties of nitrosulphocarbonate (thiocyanate) ion? What atoms of the ion change their oxidation state in the oxidation-reduction process?

Experiment 7. Reducing properties of thiocyanate ion. Obtain silver thiocyanate by an exchange reaction. Add concentrated HNO_3 to the precipitate. Check the solution for the presence of the SO_4^{2-} and CNS^- ions. Explain your observations.

15. Distribute electrons in the CO molecule orbitals.

(a) Compare the length and energy of bonds, ionization energy, standard entropy, melting and boiling points of CO and N_2. Explain the high similarity of their physical properties.

16. Give electron configurations of the CN molecule and of the CN^- and CN^+ ions.

(a) The internuclear distance in the CN^- ion and the frequency of the valency oscillations (2080 cm^{-1}) are different from those in the CN molecule (2042 cm^{-1}). Explain why.

(b) Compare the values of the dissociation energies and explain their variation in the series CN^--CN-CN^+.

(c) The CN molecule readily converts into the CN^- ion and the $(CN)_2$ molecule. Explain why.

17. Explain why dicyan is often referred to as pseudohalogen? Illustrate your answer by reaction equations.

18. (a) Write equations for reactions by which carbon(II) oxide and cyanides are obtained from compounds of carbon(IV) and carbon(II).

(b) Give examples of reactions illustrating the reducing properties of carbon(II) compounds.

Experiment 8. Obtaining carbon(II) monoxide and its properties. (Use the hood!) Obtain CO using the apparatus shown in Fig. 22. To that end, place crystals of oxalic acid (or pour formic acid) into a flask and pour concentrated sulphuric acid into a dropping funnel. Add sulphuric acid from the funnel into the flask and heat. As soon as the air is all displaced from the flask and the outlet tube, collect the evolving gas into a test tube by displacing water from it.

(a) Light the gas collected in the test tube. Note the colour of the flame.

(b) Pass CO through a preheated $[Ag(NH_3)_2]NO_3$ solution until a precipitate falls out. (Silver ammoniate is obtained by the action of excess H_3N solution on $AgNO_3$). Explain your observations.

4.2. Silicon

19. Compare the structure and radii of silicon and carbon atoms, their ionization energies, oxidation states and stable coordination numbers.

20. (a) Using the diagram shown in Fig. 46, explain what substances are suitable to reduce silicon from its dioxide.

(b) What methods are used to obtain silicon for semiconductor industry?

Experiment 10. Obtaining silicon by the magnesium (thermal) method. Fix a test tube containing a mixture of powdered magnesium

and quartz sand (7:10 by weight) in the vertical position in a stand. First heat the mixture gently, and then heat the test tube bottom until the reaction begins. Explain your observations (magnesium silicide forms along with elementary silicon).

Cool the test tube and break it. Grind its contents thoroughly in a porcelain mortar. Keep the obtained powder for future experiments.

21. (a) Characterize the attitude of silicon to metals and nonmetals, acids and alkalis. Give examples of reactions.

(b) Silicon does not dissolve in aqua regia and dissolves in the mixture HF + HNO_3. Explain why.

Experiment 11. Attitude of silicon to acids and alkalis. (Use the hood!) (a) Examine the attitude of silicon to hydrochloric and nitric acids.

(b) Try the attitude of silicon to concentrated alkali solution. Show experimentally that hydrogen is evolved in this reaction.

22. Give examples of binary silicon(IV) compounds and describe their structure. Which of them are monomers and which are polymers?

23. Some constants of diamond, silicon and silicon carbide (carborundum) are given below:

	C (diamond)	Si	SiC
d_{ee}, nm	0.154	0.234	0.175
Sublimation point, °C	3470	1428	2600
S°_{298}, J/mole·deg	2.36	18.8	16.62
ρ, g/cm³	3.51	2.33	3.2
ΔE, eV	5.6	1.12	1.5-3.5

(a) Explain why the properties of SiC are intermediate between diamond and silicon? What is the practical importance of carborundum?

24. Give structural formulas of silicon hydrides and name them.

(a) Calculate heats of combustion and compare stabilities of SiH_4 and CH_4.

(b) Why is the occurrence of saturated silicon hydrides markedly lower than of hydrocarbons? Ethylene, acetylene, and benzene analogues to silicon are unstable. Explain why.

(c) What methods are used to obtain silanes?

Experiment 12. Obtaining silanes and their self-ignition. (Use the hood!) Add, by small portions, a mixture of silicon and magnesium silicide obtained in Experiment 10, into a beaker containing hydrochloric acid (1:1). Explain your observations. When the reaction is over, decant the liquid, and rinse precipitated silicon. Hand it over to the laboratory assistant.

25. What is the chemical nature of binary silicon(IV) compounds? Complete the following:

$$CaO + SiO_2 \rightarrow \qquad SiH_4 + KOH \rightarrow$$

$$CaS + SiS_2 \rightarrow \qquad SiCl_4 + H_2O \rightarrow$$

$$NaF + SiF_4 \rightarrow \qquad SiS_2 + H_2O \rightarrow$$

26. (a) Can reactions between $SiO_2(c)$ and HCl(g) and between $SiO_2(c)$ and HF(g) occur in normal conditions? Prove your answer by values of ΔG°_{298} of the reactions.

(b) How can silicon tetrachloride be obtained?

(c) Explain the process of glass etching with hydrofluoric acid.

Experiment 13. Synthesis of silicon tetrachloride by chlorination of a mixture of silicon dioxide with carbon. Mix 3 g of powdered quartz sand with 1 g of carbon powder and concentrated solution of dextrin into a thick paste. Make small pellets, the size of a pea, out of the paste, dry them on a ceramic dish in a drying cabinet at 100°C, and then calcine at 400-500°C in a chamotte crucible under a thick bed of coal in a muffle furnace (close the crucible with the lid or a

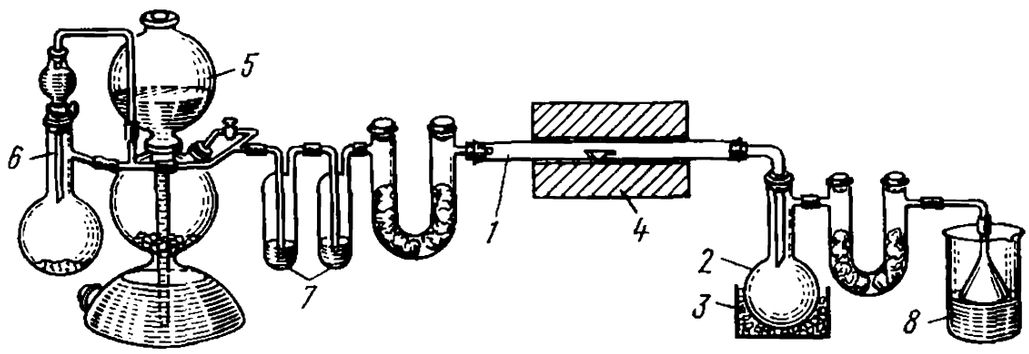

Fig. 47. Apparatus for obtaining silicon tetrachloride:

1—reaction tube; *2*—receptacle; *3*—cooling mixture; *4*—tube furnace; *5*—Kipp generator; *6*—apparatus for obtaining chlorine; *7*—concentrated sulphuric acid; *8*—water or dilute alkali

piece of asbestos). Cool the pellets slightly and transfer them into the tube *1* of the chlorinator (Fig. 47). Calcine the pellets in a flow of carbon dioxide at a temperature of 400-500°C without connecting the receptacle *2* to the apparatus.

When the mixture is positively dry, connect the receptacle *2* to the reaction tube *1*. Place the receptacle in a cooling mixture and chlorinate at 300-400°C.

When the condensation of $SiCl_4$ is over, cool the furnace without discontinuing the chlorine flow through the tube, then displace chlorine by dry carbon dioxide, disconnect quickly the receptacle, drop copper chips into it to bind excess chlorine, and stopper the vessel tightly.

27. Write the equation of hydrolysis of $SiCl_4$.

(a) Unlike hydrolysis of CF_4 and CCl_4, the hydrolysis of SiF_4 and $SiCl_4$ is an active process. Explain why.

(b) What are the products of hydrolysis of SiF_4?

Experiment 14. Hydrolysis of silicon tetrachloride. (Use the hood!) Place a few drops of $SiCl_4$ in a dish containing water. Explain your observations.

28. (a) What are unit cells of crystals of SiF_4, SiS_2 and SiO_2? Which of the compounds have an insular structure, chain structure, coordination structure?

(b) How does the melting point change in the series SiF_4-SiS_2-SiO_2?

(c) Give the melting points of SiO_2 and CO_2 and explain their marked difference.

29. Show possible combinations of the AB_4 tetrahedral unit cells in chain AB_3, band A_4B_{11}, laminar A_2B_5 and coordination AB_2 polymers.

(a) Write structural formulas of the SiO_4^{4-}, $Si_2O_7^{6-}$, $(SiO_3^{2-})_3$, $(Si_2O_5^{2-})_{2\infty}$.

(b) What is the main structural difference between the following silicate and carbonate anions? SiO_3^{2-} and CO_3^{2-}, SiS_3^{2-} and CS_3^{2-}, SiN_2^{2-} and CN_2^{2-}?

30. Examples of oxycompounds of Si(IV), P(V), S(VI) and Cl(VII) are given below:

Si (IV)	P(V)	S (VI)	Cl(VII)
SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^-
$Si_2O_7^{6-}$	$P_2O_7^{4-}$	$S_2O_7^{2-}$	$Cl_2O_7^0$
$(SiO_3^{2-})_\infty$	$(PO_3^-)_\infty$	$(SO_3^0)_\infty$	—
$(Si_2O_5^{2-})_{2\infty}$	$(P_2O_5^0)_{2\infty}$	—	—
$(SiO_2^0)_{3\infty}$	—	—	—

(a) Why does the number of possible oxycompounds increase in the series Cl(VII)-S(VI)-P(V)-Si(IV)?

(b) How does the melting point of oxides change in the series Cl_2O_7-SO_3-P_2O_5-SiO_2? Explain.

31. (a) Explain the tendency of silicic acids to form colloid solutions.

(b) Write the equation of hydrolysis of Na_2SiO_3 (the chain polymer ion SiO_3^{2-} converts into the laminar ion $Si_2O_5^{2-}$).

(c) What is the product of dehydration of silicic acids? What is the importance of this product in industry?

Experiment 15. Obtaining silicic acids in the form of gel. Add quickly 3 ml of 24 per cent solution of hydrochloric acid into a test tube containing 5 ml of concentrated solution of soluble glass and stir with a glass rod. Explain your observations.

Experiment 16. Obtaining silicic acids in the form of sol. Add 1 ml of Na_2SiO_3 solution to 6 ml of 37 per cent solution of hydrochloric acid. Heat the solution until it boils and cool. Explain your observations.

Experiment 17. Adsorption properties of silica gel. Add some crushed silica gel to copper(II) ammoniate solution and shake the mixture for a long time. Describe your observations.

Experiment 18. Hydrolysis of silicates. (a) Try Na_2SiO_3 solution with litmus.

(b) Mix Na_2SiO_3 solution (1-2 ml) with two volumes of NH_4Cl solution. (Use the hood!) Identify the evolving gas. Explain your observations.

32. Figure 48 shows dimeric representation of the structure of crystalline and vitreous quartz and sodium silicate glass.

(a) What is the difference between the crystal and vitreous (amorphous) states?

(b) Explain why thermal and mechanical strength of sitalls (glass-ceramic) differ sharply from those of ordinary lime glass?

(c) How does the difference in solubility of SiO_2 and Na_2SiO_3 agree with their structure?

(d) How does the solubility of silicates change with replacement of the Na^+ ion by the Ca^{2+}, Pb^{2+}, Fe^{2+} ions?

(e) Write equations of the reactions for obtaining window glass.

Experiment 19. Obtaining insoluble silicates. Pour 120-150 ml of 10 per cent Na_2SiO_3 solution into a 250-ml beaker and add a few

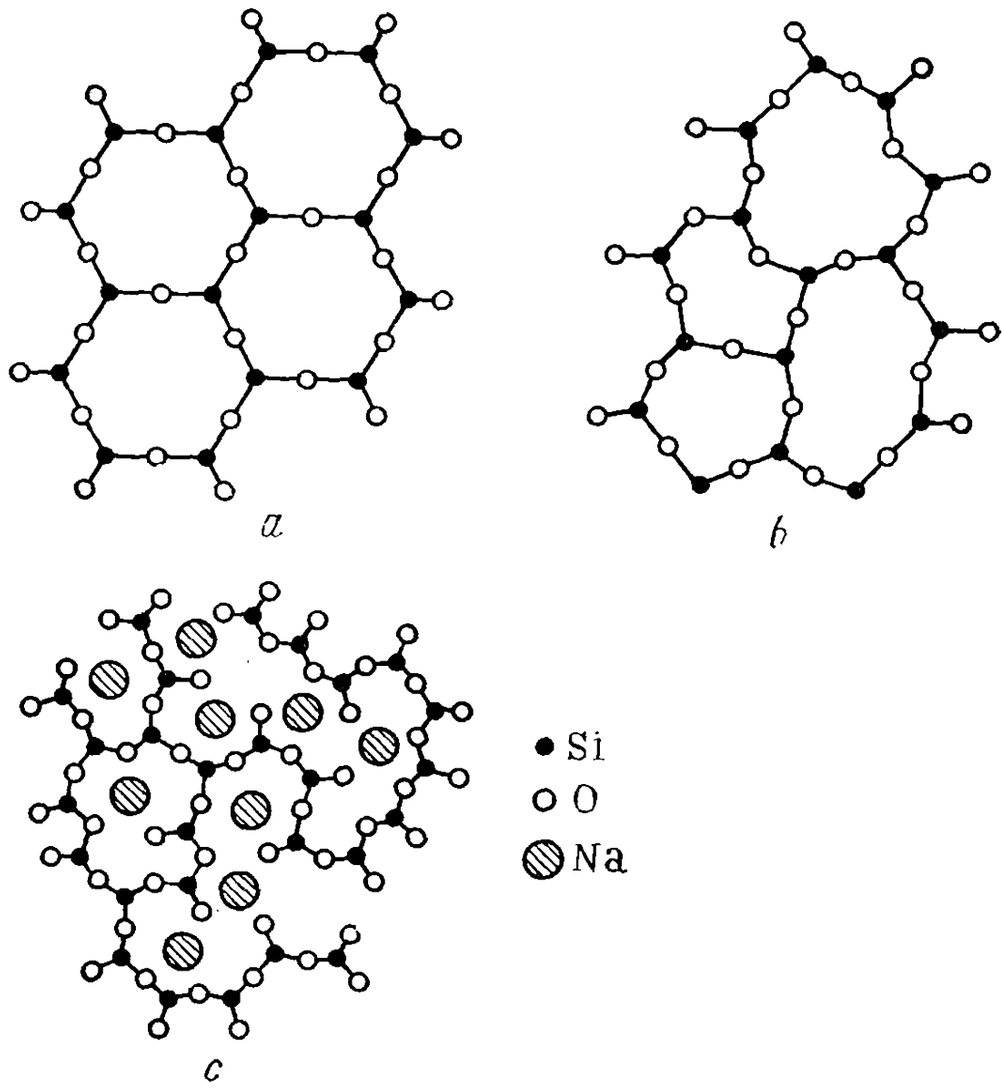

Fig. 48. Dimeric representation of the structure of the crystalline (*a*) and vitreous (*b*) quartz and sodium silicate glass (*c*)

crystals (size of a wheat grain) of $CuSO_4 \cdot 5H_2O$; $NiSO_4 \cdot 7H_2O$; $Co(NO_3)_2 \cdot 6H_2O$; $FeSO_4 \cdot 7H_2O$; $MnSO_4 \cdot 4H_2O$; $Pb(NO_3)_2$; $ZnSO_4 \times \times 7H_2O$.

Note the intricate form of precipitated insoluble silicates. Explain.

33. (a) Calculate ΔG°_{298} of the formation of $CaCO_3$(c) and of $CaSiO_3$ (c) from the oxides. What oxide, CO_2 or SiO_2, has stronger acid properties?

(b) Calculate ΔG°_{298} of the reaction between $CaCO_3$(c) and SiO_2(c). Under what conditions does the reaction occur? At what temperature $p_{CO_2} = 101.325$ kPa? Which of the oxides, CO_2 or SiO_2, has stronger acid properties in this case? Explain.

(c) Give the values of the ionization constants and compare the strength of carbonic and silicic acids.

Experiment 20. Comparing strength of carbonic and silicic acids. Pass CO_2 into Na_2SiO_3 solution. Explain your observations.

Experiment 21. Hydrolysis of glass. Heat an end of a glass tube until it softens and plunge quickly into water: the glass cracks. Decant the water from the beaker, transfer the crushed glass into a porcelain dish and grind to powder. Add 2-3 drops of phenolphthalein. Write the equation of hydrolysis of glass assuming that Na_2SiO_3 is hydrolyzed.

4.3. Germanium Subgroup Elements

34. Show graphically the variation of the orbital atomic radius and ionization energy with the atomic number of the *p*-elements of group IV. Explain the curves.

35. (a) What are the oxidation states of germanium, tin and lead and which of them are more characteristic?

(b) Explain the variation of the stable oxidation state in the series C-Si-Ge-Sn-Pb.

36. Describe the structure of germanium, tin and lead.

(a) How do the structure, coordination atomic numbers, type and energy of chemical bond change in the series C-Si-Ge-Sn-Pb?

(b) Construct and explain a graph showing the variation of the standard entropy and hardness of simple substances with the atomic number of *p*-element of group IV.

	C (diamond)	Si	Ge	Sn(β)	Pb
Hardness (diamond 10)	10	7	6	1.8	1.5

How does the variation of hardness and of the standard entropy in the series C (diamond)-Si-Ge-Sn(β)-Pb agree with the structure of the elements?

37. Figure 49 shows the variation of entropy and enthalpy of lead with temperature.

(a) Explain the curves.

(b) How do the values of ΔH_{melt} and ΔS_{melt} change in the series C-Si-Ge-Sn-Pb? Explain.

(c) How does the melting point of the simple substances change with increasing atomic number of *p*-elements of group IV? Explain.

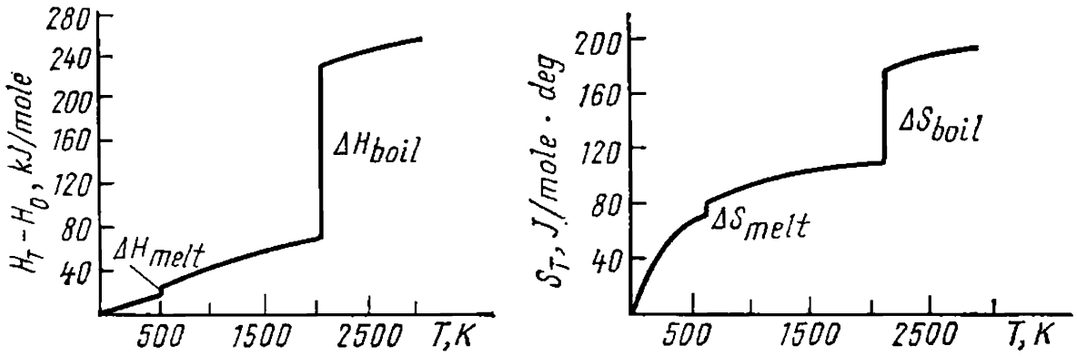

Fig. 49. Variation of enthalpy and entropy of lead with temperature

38. (a) How does the width of the forbidden zone change in the series C-Si-Ge-Sn-Pb?

(b) Semiconductors of what type (*p* or *n*) are formed if Sb is added to Ge, In to Si and Se to Ge?

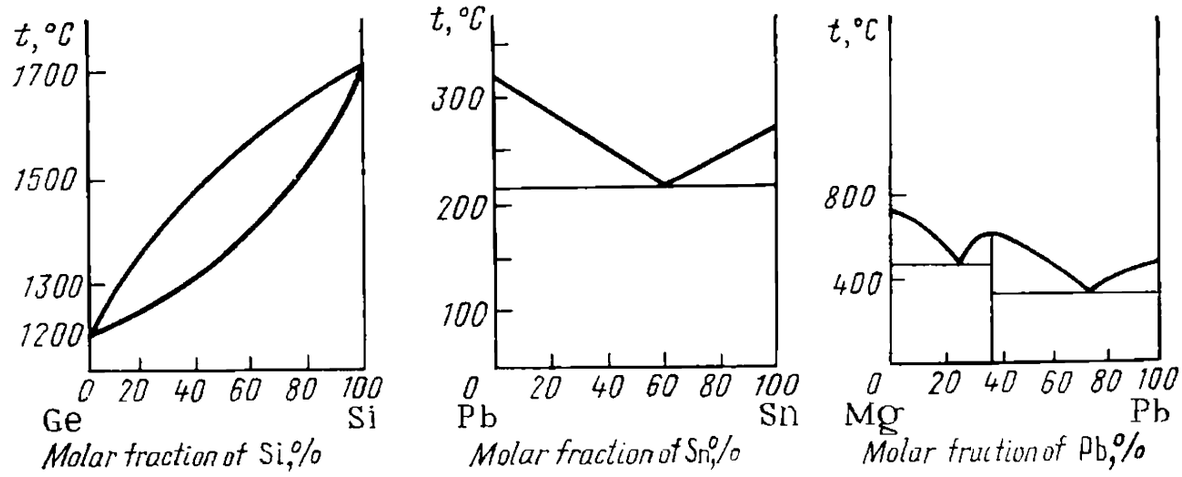

Fig. 50. Phase diagram of the systems Si-Ge, Sn-Pb, and Mg-Pb

39. (a) Explain the difference between the phase diagrams shown in Fig. 50.

(b) What is the practical importance of tin alloys with lead?

Experiment 22. Thermal analysis of the tin-lead system. Melt separately lead and tin in a crucible furnace and determine their crystallization points using a thermocouple. Prepare a eutectic mixture of tin and lead, melt it, and determine the crystallization point. Using the obtained data, construct a simplified phase diagram of the system Sn-Pb.

40. Using Fig. 46 explain:

(a) Which of the simple substances given in the diagram can reduce tin and lead from their oxides?

(b) At what temperature can carbon be used as a reductant to obtain lead from PbO, tin from SnO_2, germanium from GeO_2?

(c) What methods are used to obtain germanium of special purity for semiconductor industry?

Experiment 23. Obtaining lead by reducing its oxide with carbon. Make a depression in a piece of charcoal and fill it with a mixture (1:1) of powdered coal and PbO (or PbO_2). Put a blowpipe into the reducing part of the flame of a burner and blow carefully to direct the flame of the burner onto the border between coal and the mixture. Continue the reduction process until a drop of molten metal is seen.

41. Compare the values of $E^\circ_{Sn^{4+}/Sn}$ and $E^\circ_{Zn^{2+}/Zn}$. Can zinc be used to displace tin from solution of its tetrachloride?

Experiment 24. Obtaining tin and germanium by their reduction with zinc. (a) Put a plate of metallic zinc into $SnCl_4$ solution. Explain your observations.

(b) Put a zinc granule into an acidified solution of $K_2[GeF_6]$. Explain precipitation of a dark-brown sponge-like substance.

42. Give examples of reactions illustrating the increasing metallic character in the series Ge-Sn-Pb.

43. Show graphically the variation of length and energy of bond, enthalpy of formation of simple hydrogen compounds of the *p*-elements of group IV with the atomic number of the elements.

(a) Explain the curves.

(b) Why does the number of probable hydrogen compounds sharply decrease in the transition from C to Pb?

(c) What reaction underlies the general method of obtaining hydrogen compounds of the *p*-elements? Give equations of reactions of obtaining germanes, stannanes and plumbanes.

44. According to available data, the coordination number in the subgroups of the *p*-elements increases with the atomic number, for example:

CO_3^{2-}	NO_3^-	—	—
SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^-
$GeO_4^{4-}(GeO_6^{8-})$	AsO_4^{3-}	SeO_4^{2-}	BrO_4^-
SnO_6^{8-}	SbO_6^{7-}	TeO_6^{6-}	IO_6^{5-}
PbO_6^{8-}	—	—	—

(a) What unit cells form oxycompounds of germanium (IV) and tin (IV)?

(b) Explain why the composition and structure of oxygermanates are more varied than those of oxysilicates?

(c) What is the structure type of GeO_2, SnO_2 and PbO_2 crystals?

45. Figure 51 shows the phase diagram of the system Li_2O-GeO_2.

(a) What is the composition of oxygermanates formed in the series? Describe their structure. (The oxygermanates are isotypical to the corresponding silicates.)

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(b) $BaSnO_3$ and $SrSnO_3$ crystals have the perovskite structure. What is the structure of the SnO_3^{2-} ion in these compounds?

46. The I-R spectra of $Na_2SnO_3 \cdot 3H_2O$ show the absence of deformation oscillations of the H—O—H bonds and the presence of those of the Sn—O—H bonds.

(a) Explain the structure of this compound.

(b) Under what conditions do EO_2 and $E(OH)_4$ form oxygermanates, hydroxygermanates, stannates and plumbates? Give examples of the reactions.

Experiment 25. Obtaining tin(IV) hydroxide and studying its amphoteric properties. Add ammonia solution to tin tetrachloride solution. Try the attitude of the solution obtained to hydrochloric acid and to excess alkali. Explain your observations.

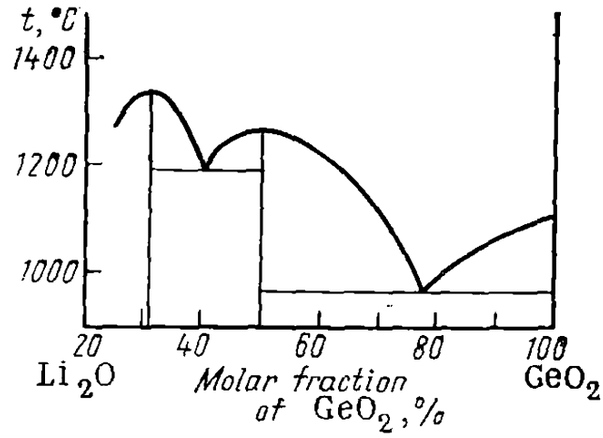


Fig. 51. Phase diagram of the system Li_2O-GeO_2

47. According to available data, tin(IV) hydroxide has a variable composition and ages on standing, heating or at increasing pH.

(a) Explain this phenomena.

(b) What is the difference between the chemical activity of α- and β-stannic acids?

Experiment 26. Ol and oxol derivatives of tin(IV). Obtain tin(IV) hydroxide. Boil the solution with the precipitate. Try the attitude of the precipitate to concentrated hydrochloric acid. Compare your observations with the result of Experiment 25.

48. Give examples of reactions illustrating acid-base properties of disulphides of tin and germanium.

Experiment 27. Obtaining tin disulphide and its properties. (Use the hood!) Obtain SnS_2 by an exchange reaction. Try its attitude to dilute HCl and excess $(NH_4)_2S$ solution. Try the attitude of the solution of the thio salt to dilute hydrochloric acid. Explain your observations.

49. (a) Explain the sharp elevation of the melting point in the series from GeF_4 to SnF_4, from SnF_4 to $SnCl_4$ and from PbF_4 to $PbCl_4$.

(b) What are the acid-base properties of tetrahalides? Illustrate your answer by equations of reactions.

(c) All halide complexes of lead(IV), $PbHal_6^{2-}$, are known and all of them are sufficiently stable, while $PbCl_4$ is unstable and $PbBr_4$ and PbI_4 are not known. Explain.

Experiment 28. Obtaining $SnCl_6^{2-}$ derivatives. Place a drop of $SnCl_4$ into a test tube containing concentrated hydrochloric acid and add a saturated solution of KCl. Explain precipitation.

Experiment 29. Synthesis of ammonium hexachloroplumbate. (Use the hood!) Saturate a solution of $PbCl_2$ in concentrated hydro-

chloric acid (cooled in ice) with chlorine. Add NH_4Cl to the solution. Separate the precipitate and dry. Add water to a part of the compound obtained. Explain precipitation of a dark-brown substance. Compare the stability of the $SnCl_6^{2-}$ and $PbCl_6^{2-}$ ions to hydrolysis.

50. Write the equation of hydrolysis of $SnCl_4$.

Experiment 30. Hydrolysis of tin tetrachloride. Explain the appearance of white fume when the bottle containing $SnCl_4$ is opened.

Experiment 31. Solubility of lead(II) compounds. Give solubility products of carbonate, nitrate, chloride, iodide, sulphate, acetate, hydroxide and sulphide of lead(II) in water. Check if it is possible to obtain these compounds by exchange reactions. Note the colour of these compounds.

51. Water-insoluble $PbCl_2$ and $Pb(OH)_2$ dissolve in excess concentrated hydrochloric acid and alkali respectively. Explain.

Experiment 32. Amphoteric properties of tin(II) and lead(II) hydroxides. Obtain hyroxides of Sn(II) and Pb(II) and try their amphoteric properties.

Experiment 33. Formation of chlorine complexes of lead(II). Obtain $PbCl_2$ and transfer a small amount into a test tube containing concentrated hydrochloric acid by a glass rod. Explain dissolution of the precipitate.

52. Using the results of Problem 51 and Experiment 31, explain the attitude of lead to nitric, hydrochloric, sulphuric acids and alkalis. How do germanium and tin act under these conditions?

Experiment 34. Attitude of tin and lead to acids and alkalis. Try the action of tin and lead on acids and alkalis in the cold and with heating.

53. Calculate ΔG°_{298} of the processes

$$EO_2(c) + E(c) = 2EO(c) \quad (E = Ge, Sn, Pb)$$

(a) Draw your own conclusion on stable oxidation states of the elements in the germanium subgroup.

(b) Give examples of reactions to illustrate the presence of reducing properties in tin (II) compounds and the oxidizing properties in lead(IV) compounds.

Experiment 35. Reducing properties of tin(II) compounds.

(a) Carry out a reaction between $SnCl_2$ and $FeCl_3$ solutions. Explain your observations.

(b) Obtain sodium hydroxystannate(II) solution and add by drops $Bi(NO_3)_3$ solution. Explain the formation of precipitate.

Experiment 36. Oxidizing properties of lead(IV) compounds. (Use the hood!) Add 2-3 ml of concentrated nitric acid into a test tube containing a grain of minium or lead dioxide and boil the mixture. Add 2-3 drops of Mn(II) compound solution into the test tube. Boil the mixture again. Allow the solution to stand and observe the red-violet colour (MnO_4^- ion) of the solution. Make out the reaction equation.

Experiment 37. Comparing the reducing property of tin(II) and lead(II) compounds. (Use the hood!) Obtain sulphides of tin(II) and lead(II). Try them in a reaction with $(NH_4)_2S_2$. Explain your observations.

Experiment 38. Obtaining lead dioxide. Add chloride of lime to $Pb(CH_3COO)_2$ solution. Heat the mixture. Explain precipitation of a coloured substance.

CHAPTER 5

p-Elements of Group III

5.1. Boron

1. Using the theory of valency bonding, show hybrid states of valency orbitals, coordination numbers and unit cells characteristic of boron.

2. (a) What simple substances can be used as reductants to obtain boron from its oxide (see Fig. 46)?

(b) What methods are used to obtain boron of special purity?

Experiment 1. Obtaining boron by magnesium-thermal method from its oxide. (Use the hood!) Obtain B_2O_3 by dehydrating H_3BO_3. To that end, heat an iron crucible containing H_3BO_3, first carefully then over a strong flame. Cool the mass obtained, grind it thoroughly in a mortar and mix with two weights of magnesium powder.

Place the mixture in the crucible and heat over a burner (observe the reaction through the glass of the hood). Allow the dark mass to cool and treat it with dilute hydrochloric acid in a beaker. Separate the precipitated boron, rinse it and dry.

3. (a) What is the polarizing action of B^{3+} ion and can it exist in the hydrated form in a solution?

(b) What complexes, cation or anion, are more characteristic of boron(III)?

(c) Describe the attitude of boron to acids and alkalis.

Experiment 2. Oxidation of boron with nitric acid. (Use the hood!) Place a grain of boron into a porcelain dish and add 65 per cent nitric acid. Evaporate the mixture on a water bath until crystallization begins. Explain your observations.

4. Name the elements in combination with which boron has the positive oxidation state.

(a) What binary compounds and the corresponding anion complexes of boron(III) are monomolecular and what are polymers?

(b) Give examples of reactions to illustrate the acid-base properties of binary compounds of boron(III).

5. Give examples of hydrogen compounds of boron.

(a) Explain the structure of B_2H_6 molecule and the emission of energy ($\Delta H^\circ_{298} = -117$ kJ/mole) during its formation from BH_3.

(b) Explain the structure of the B_4H_{10} molecule.

6. Compare the heat of combustion of 1 kg of diborane and of ethane.

(a) Explain the marked difference between the heats of combustion of these compounds.

(b) What is the practical importance of combustion of boron hydride?

7. The affinity of the BH_3 molecule for the hydride ion is very high ($\Delta H^\circ_{298} = -314$ kJ/mole).

(a) Explain the mechanism of formation of BH_4^- from BH_3.

(b) Give examples of formation of other boron hydride (boranate) ions.

(c) What properties of boron hydrides account for their use in chemical analysis and synthesis?

Experiment 3. Reducing properties of boron hydrides. Place $K[BH_4]$ into a test tube containing $CuSO_4$ solution. Explain precipitation.

8. Construct a graph showing the variation of bond length and energy, and force constant of bonding of boron trihalide molecules with the atomic number of the halogens.

(a) Explain the curves.

(b) Explain variation of ΔH_f in the series BF_3-BCl_3-BBr_3-BI_3.

(c) Give the melting and boiling points of $BHal_3$ and explain $BHal_3$ states of aggregation in normal conditions.

9. Calculate ΔG°_{298} and ΔG°_{573} of obtaining BCl_3 by the reaction between boron oxide, graphite and chlorine.

(a) How does the possibility of the reaction depend on temperature?

(b) What factor, enthalpy or entropy, determines this reaction?

Experiment 4. Synthesis of boron trichloride. (Use the hood!) Assemble an apparatus as shown in Fig. 47. Place 3 g of amorphous boron into a porcelain boat and put it into a furnace. Dry thoroughly the apparatus by blowing carbon dioxide through it without connecting the receptacle *2* to the reaction tube *1*. Heat the furnace to 100°C. When water vapour stops evolving, raise the temperature in the furnace to 400-500°C. Connect the receptacle cooled with dry ice to the apparatus. Pass a strong current of dry chlorine through the apparatus. When the reaction is over, stop heating and displace chlorine from the apparatus by carbon dioxide. Disconnect the receptacle, stopper it by a plug through which a thermometer is passed and distil the receptacle contents into a long (30 cm) test tube cooled with dry ice. (If BCl_3 is green, add copper chips.)

10. Boron trihalides and organic derivatives of the BR_3 type can attach H_3N, NR_3 and H_2O molecules.

(a) Explain this fact.

(b) Explain the structure of compounds of the following composition: $BF_3 \cdot NH_3$ and $BF_3 \cdot H_2O$.

(c) Make out equations of hydrolysis of BF_3 and BCl_3. What is the difference between the products of hydrolysis of these compounds?

Experiment 5. Hydrolysis of boron trichloride. Explain the appearance of white fume when the bottle containing BCl_3 is opened.

11. BF bond length in BF_3 is less (0.129 nm) than that in BF_4^- (0.143 nm).

(a) Explain this experimental fact.

(b) Under what conditions does BF_3 convert into BF_4^-? Write equations of formation of tetrafluoroborates.

Experiment 6. Synthesis of ammonium tetrafluoroborate. (Use the hood!) Add 3.3 g of NH_4HF_2 and 1.3 g of H_3BO_3 to 10 ml of water in a plastic dish. Heat the mixture on a water bath with stirring by a plastic rod until the solution is completely clear. Cool the solution: long colourless crystalline needles precipitate. Separate them on a Büchner funnel. Explain your observations.

12. Figure 52 shows a phase diagram of the system B_2O_3-H_2O.

(a) What is the composition of compounds formed in this system?

(b) Write the hydration of B_2O_3 by steps.

(c) What form of boric acid is most stable in aqueous solutions?

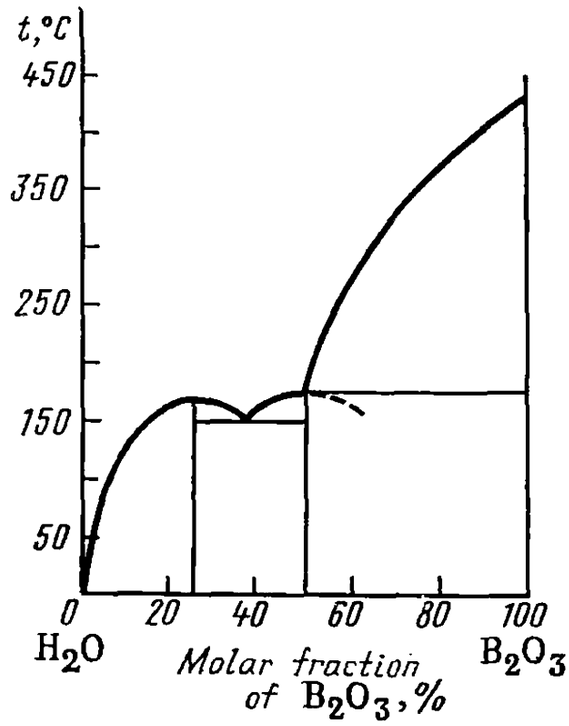


Fig. 52. Phase diagram of the system B_2O_3-H_2O

Experiment 7. Hydration of boron(III) oxide. Keep boron(III) oxide in air and observe.

13. The mean internuclear distance d_{BO} of boron(III) oxycompounds is 0.136 nm in triangular unit cells (BO_3) and 0.148 nm in tetrahedral ones (BO_4).

(a) Explain the difference between d_{BO} in BO_3 and BO_4 unit cells.

(b) Describe the structure of the H_3BO_3 molecule and of boric acid crystals using the following data. Hydrogen orthoborate is lustrous oily scales under normal conditions. The length of the BO bond is 0.136 nm, the distance between boron atoms in a layer is 0.272 nm, and the interlayer distance is 0.318 nm.

(c) What is characteristic of ionization of boric acid in aqueous solutions? Characterize its strength.

Experiment 8. Studying acid properties of H_3BO_3. Measure the pH of H_3BO_3 solution using a pH-meter. What is the colour of litmus in the solution?

14. Esters have been found in the products of reaction of H_3BO_3 with alcohols. What properties of H_3BO_3, acid or base, are proved by this fact?

Experiment 9. Obtaining ester of orthoboric acid (qualitative test for boron compounds). Place crystals of borax (at the end of a spatula)

into a crucible, wet them with concentrated sulphuric acid (density, 1.84 g/cc) and add 2-3 ml of ethyl (methyl) alcohol. Stir the mixture with a glass rod and light the evolving ester. Note the colour of the flame.

15. When the pH of a hydrogen orthoborate solution increases, polymerization takes place, and polyborate ions, for example the tetraborate ion, $[B_4O_5(OH)_4]^{2-}$, are formed.

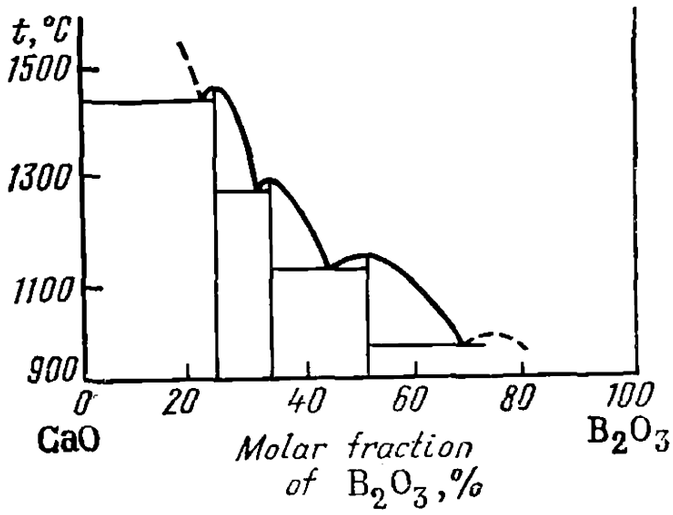


Fig. 53. Phase diagram of the system $CaO-B_2O_3$

(a) What is the structure of this ion (the length of the BO bond is 0.136 and 0.148 nm)?

(b) How can sodium tetraborate be obtained from orthoboric acid?

(c) What compound is formed if acid is added to sodium tetraborate (borax) solution?

Experiment 10. Obtaining sodium tetraborate from hydrogen orthoborate. Place a saturated solution of orthoboric acid and soda into a porcelain dish. Boil the solution until carbon dioxide stops evolving and evaporate the remainder until crystals precipitate. Separate the crystals on a Büchner funnel.

Experiment 11. Obtaining hydrogen orthoborate from tetraborates. Dissolve 5 g of borax in 10 ml of water in a beaker with heating, and add 26 per cent hydrochloric acid (density, 1.13 g/cc) to the solution. (Take excess quantity of the acid as compared with the theoretically required amount.) Cool the solution slowly: crystals precipitate. Separate them on a Büchner funnel and wash with cold water.

16. Figure 53 shows the phase diagram of the system $CaO-B_2O_3$.

(a) Explain the great variety of oxyborates known.

(b) What structure units compose the BO_2^- ions of $NaBO_2$ and $Ca(BO_2)_2$ crystals if $d_{BO} = 0.137$ nm? Draw a structural formula of the trimetaborate ion ($NaBO_2$ crystal) and the polymetaborate ion [$Ca(BO_2)_2$ crystal].

Experiment 12. Obtaining metaborates and their solubility. Add solutions of salts of Ca^{2+} and Pb^{2+} to a solution of borax. Write the equations of the reactions assuming that metaborates are formed in them.

17. (a) Explain the easiness of the transition of boron oxide and oxyborates into the vitreous state. Can vitreous B_2O_3 be used as a construction material?

(b) What properties does B_2O_3 give to silicate glass?

Experiment 13. Obtaining high-molecular vitreous metaborates. Obtaining coloured borax pearls. Heat a loop of a platinum wire in

an oxidizing flame of a burner and touch on crystals borax (boric acid) with it. Heat the crystals on the wire loop in the flame to melt them. Plunge the wire with the vitreous polymetaborate into a solution of a cobalt salt in a test tube and heat again to melting. Explain your observations.

Carry out similar experiments with salts of chromium and nickel.

18. The polymorphic conversion of graphite-like boron nitride into its diamond-like form is accompanied by the change in the frequency of the valency oscillations of the BN bond and in its length:

	$\tilde{\nu}_{BN}$, cm^{-1}	d_{BN}, nm
$BN_{diamond}$	1140	0.158
$BN_{graphite}$	1385	0.144

How do these facts agree with the structure of these modifications of boron nitride?

19. Below are given some characteristics of borazole and its derivatives and of the corresponding carbon analogues:

	$B_3N_3H_6$	$B_3N_3H_5CH_3$	$B_3N_3H_3(CH_3)_3$
M	80.5	94.5	122.6
M. p., °C	−58	−59	31.5
B. p., °C	55	87	129

	C_6H_6	$C_6H_5CH_3$	$C_6H_3(CH_3)_3$
M	78.1	92.1	120.1
M. p., °C	5.5	−95	−50
B. p., °C	80	111	165

(a) Give structural formulas of the compounds specified.

(b) Explain the marked similarity of borazole and its derivatives with the corresponding carbon analogues.

5.2. Aluminium

20. What coordination numbers and the corresponding unit cells are characteristic of aluminium?

21. Figure 46 shows the variation of the Gibbs free energy of formation of some oxides with temperature. Examine the graph and answer the following questions:

(a) What is the practical importance of the high affinity of aluminium to oxygen? Give examples of aluminothermy reactions?

(b) Is it reasonable to obtain aluminium from its oxide by chemical reduction?

(c) How is aluminium obtained in industry?

Experiment 14. Burning of aluminium powder. (Use the hood!) Introduce aluminium powder into the flame of a burner on the end of a spatula and overturn it. Explain your observations.

Experiment 15. Aluminothermy. (Use the hood!) Place thermit (a mixture of dry powders of Fe_3O_4 (25 per cent) and Al (75 per cent)) into a refractory crucible, add (in the centre) the ignition mixture and fix a magnesium ribbon in it. (Prepare the ignition mixture from powdered aluminium and Na_2O_2 or BaO_2 taken in the ratio of 1 : 1.) Place the crucible on an asbestos sheet in the hood, and light the magnesium behind the screen. Explain your observations. What is the practical importance of thermit?

22. (a) Compact aluminium has a dull lustre. Why?

(b) How does aluminium react with concentrated nitric and sulphuric acid?

Experiment 16. Detecting the oxide film on aluminium surface. Heat an aluminium wire in the flame of a burner till it melts. The molten metal does not separate from the wire. Explain why.

Experiment 17. Effect of the oxide film on the chemical activity of aluminium. Polish two aluminium plates with emery paper and remove fat by alcohol. Place a drop of $Hg(NO_3)_2$ or $HgCl_2$ onto one plate and observe the formation of amalgam (alloy of Al and Hg). Then try the attitude of both plates to water in the cold and with heating.

Experiment 18. Reaction of aluminium with acids and alkalis. Try aluminium with acids and alkalis of different concentration. Pay attention to the absence of a visible reaction.

Experiment 19. Passivating aluminium. Hold an aluminium plate in a 10 per cent $K_2Cr_2O_7$ solution for 5 minutes and then wash it. Try the attitude of the plate to hydrochloric acid. Explain the decreased chemical activity of aluminium after treatment in the dichromate.

23. The reaction of aluminium with iodine is accompanied by the decrease in the Gibbs free energy ($\Delta G_f^\circ = -304$ kJ/mole AlI_3). The reaction does not occur practically in the absence of water. Why?

Experiment 20. Reaction of aluminium with iodine in the presence of water. (Use the hood!) Place a dry mixture of powdered aluminium and iodine (1 : 12) in a heap on a gauze with an asbestos centre and add a few drops of water. Explain your observations.

24. Describe the structure of aluminium trihalides.

(a) Explain the character of variation of density, standard entropy, melting point and enthalpy of formation in the series AlF_3-$AlCl_3$-$AlBr_3$-AlI_3.

(b) Why does the solubility of AlF_3 in water (0.559 g/100 g H_2O at 25°C) differ greatly from that of $AlCl_3$ (44.38 g/100 g H_2O at 25°C)?

25. Write the equations for synthesis of fluoride and chloride of aluminium(III) from Al_2O_3.

Experiment 21. Synthesis of aluminium trichloride. Assemble the apparatus as shown in Fig. 54. Place 2-3 grains of aluminium into a boat and put it into the reaction tube *1*. Pass continually dry hyd-

rogen chloride through the apparatus and heat the reaction tube to 600-800°C. When sufficient quantity of aluminium chloride is collected in the receptacle *2*, cool the apparatus. (Pass dry air instead

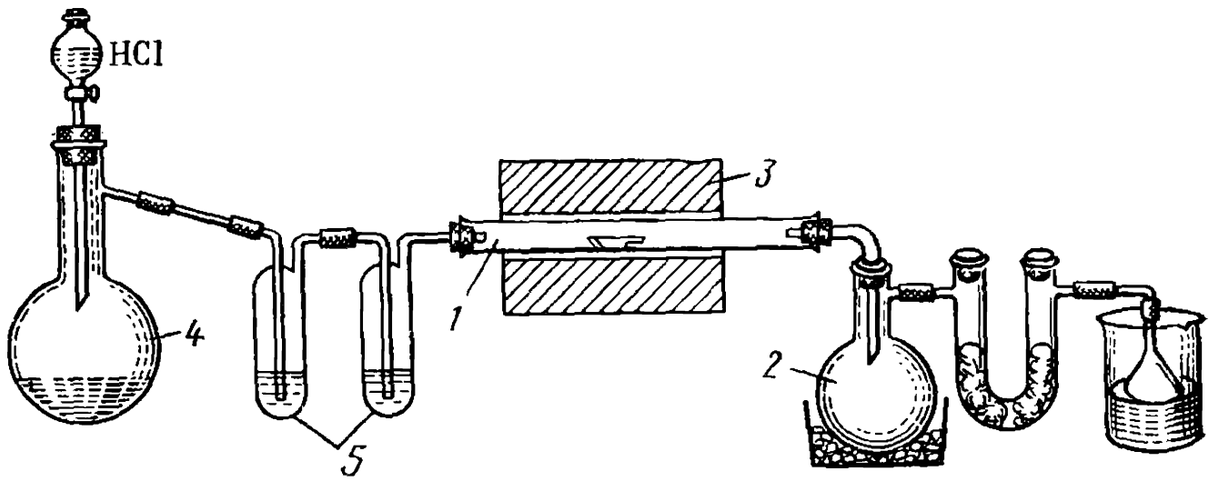


Fig. 54. Apparatus for synthesizing $AlCl_3$:
1—reaction tube; *2*—receptacle; *3*—tube furnace; *4*—HCl; *5*—concentrated sulphuric acid

of hydrogen chloride.) When the apparatus is cooled, disconnect the receptacle *2* and stopper it quickly with rubber.

26. Consider the phase diagrams for the systems MCl-$AlCl_3$ (see [1], Fig. 133).

(a) What compounds are formed in the system? Describe their structure.

(b) What properties, acid or base, characterize $AlCl_3$ in the reaction with halides of the *s*-elements of group I?

(c) How does the stability of the compounds vary in the series? Explain.

(d) What chemical compounds are formed by fusion of NaF with AlF_3 (Fig. 55)? Describe their structure.

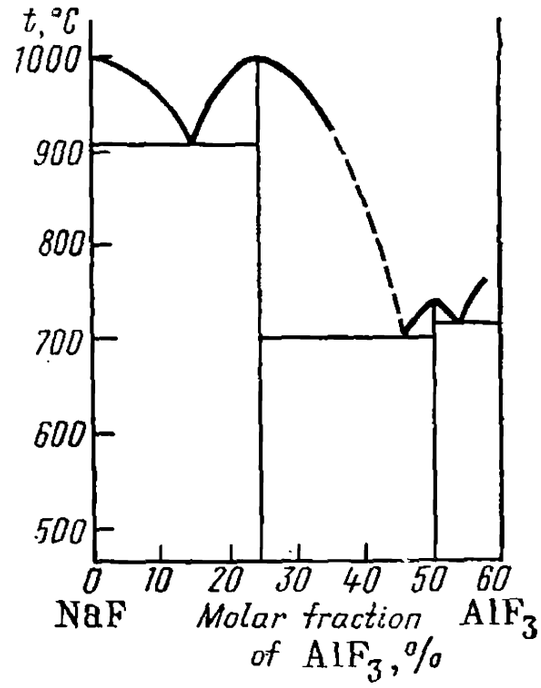


Fig. 55. Phase diagram of the system NaF-AlF_3

Experiment 22. Formation of aluminium fluoride complexes in solution. Place AlF_3 into a test tube containing water. Explain the dissolution of AlF_3 when NaF is added.

27. Make out equations of reactions of KF(c) with the following compounds: BF_3(g), AlF_3(c), SiF_4(g) and MgF_2(c).

(a) Characterize the acid-base activities of AlF_3 with respect to KF as compared with BF_3 and also MgF_2 and SiF_4.

(b) How does it agree with the position of B and Al, Mg and Si in the periodic system?

28. Make out equations of reactions of AlH_3, Al_2O_3, AlN, Al_2S_3 with similar compounds of potassium.

(a) What properties, base or acid, of binary compounds of Al(III), are demonstrated by these reactions?

29. (a) Calculate ΔG°_{298} of the interaction of Al_2O_3(c) and B_2O_3(c) with CaO(c). Which of the oxides, Al_2O_3 or B_2O_3, has stronger acid properties and how do acid properties depend on the position of boron and aluminium in the periodic system?

(b) How do acid properties change in the series H_3BO_3-$Al(OH)_3$? Give examples of reactions illustrating the acid-base properties of $Al(OH)_3$.

(c) Calculate ΔG°_{298} of reactions of Al_2O_3(c) with SO_3(c) and with Na_2O(c). What function, acid or base, prevails in Al_2O_3 in these reactions?

Experiment 23. Obtaining aluminium hydroxide and its amphoteric properties. Obtain $Al(OH)_3$ and examine its attitude to acids, alkalis and ammonia solution. Make your conclusions concerning the chemical nature of $Al(OH)_3$.

30. (a) Compare the equations of hydrolysis of $AlCl_3$ and BCl_3.

(b) How does the degree of hydrolysis of aluminium compounds depend on the nature of the anion? Can $Al_2(CO_3)_3$ be obtained by an exchange reaction?

Experiment 24. Hydrolysis of aluminium(III) compounds. Add water, by drops, to $AlCl_3$ and watch the reaction. Determine experimentally the reaction (pH) of the solution. Determine the reaction of $Al_2(SO_4)_3$ and $Al(NO_3)_3$ solutions.

31. Compare ΔG°_{298} of the formation of Al_2S_3 from the simple substances, and from ions in aqueous solution. Can Al_2S_3 be obtained in an aqueous solution by an exchange reaction?

Experiment 25. Obtaining aluminium sulphide. Place 1-2 g of aluminium shavings into a porcelain crucible, close the crucible with a lid and place it on a porcelain triangle in the stand. (Use the hood, observe the reaction through the glass screen!) Heat the crucible over a burner. Taking all precautions, take sulphur by tongs and drop it into the crucible. Put aside the burner: the temperature of the crucible can rise sharply due to the reaction. Add another lump of sulphur, then still another, etc., until the mass stops developing high temperature. Allow the crucible to cool, remove its contents (Al_2S_3), place it into a test tube and stopper.

Experiment 26. Hydrolysis of aluminium sulphide. (Use the hood!) Act with several drops of water on a grain of Al_2S_3. Explain your observations. Check experimentally the possibility of formation of aluminium sulphide by an exchange reaction in solution. Identify experimentally the compound formed in this reaction.

5.3. Elements of the Gallium Subgroup

32. Show graphically the variation of atomic radii and the first ionization energy of *p*-elements of group III with their atomic number. Explain the curves.

33. Figure 56 shows the phase diagrams of some systems.

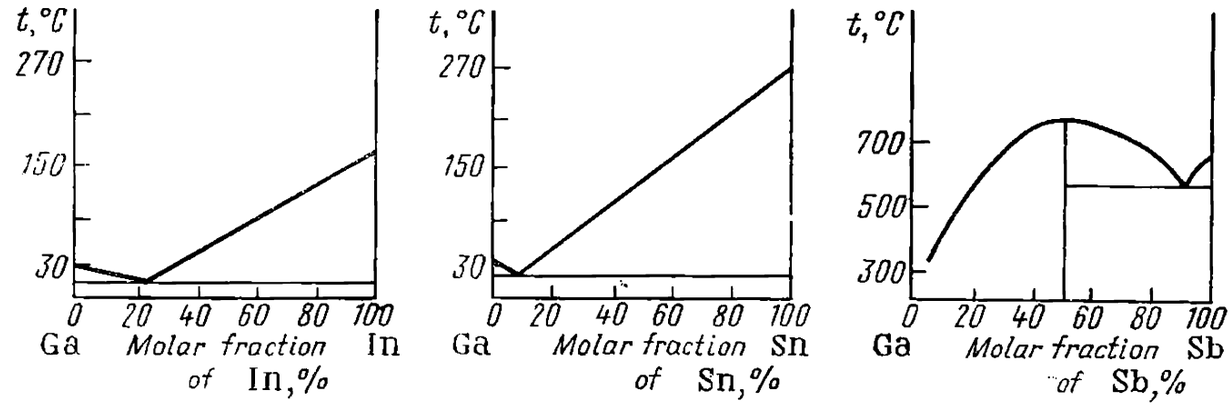


Fig. 56. Phase diagrams of the systems Ga-In, Ga-Sn, Ga-Sb

(a) Explain the difference in the phase diagrams of the systems Ga-In and Ga-Sn on the one hand and of the system Ga-Sb on the other hand.

(b) What is the composition of the eutectics Ga-In and Ga-Sn?

(c) The alloys given below melt at low temperature. Explain why.

Alloy composition (molar fraction, %)	m. p. °C
Ga, 77.6; In, 22.4	16.5
Ga, 95; Sn, 5	20
Ga, 60.8; In, 24.5; Sn, 12.7; Ag, 2	9.2

(d) Explain the low melting point of gallium. What is the practical importance of the great difference between the melting and boiling points of gallium?

Experiment 27. Melting gallium. Place a piece of gallium in a test tube and heat on a water bath at 40°C. Observe melting of the metal.

34. Explain the great difference between melting points of GaF_3 (1000°C) and $GaCl_3$ (78°C), InF_3 (1172°C) and $InCl_3$ (586°C).

35. Figure 57 shows phase diagrams of some systems.

(a) What compounds are formed in these systems?

(b) What acid-base properties of $InCl_3$ are demonstrated in reactions with halides of *s*-elements and of thallium(I)?

36. Calculate ΔG°_{298} of reactions occurring according to the equation

$$E(OH)_3(c) + 3H^+(sln) = E^{3+}(sln) + 3H_2O(l)$$

(E = Al, Ga, In)

(a) How do the acid-base properties change in the series $Al(OH)_3$-$Ga(OH)_3$-$In(OH)_3$?

(b) How do the properties of the hydroxides depend on the size of the Al^{3+}, Ga^{3+}, and In^{3+} ions?

Experiment 27. Hydroxides of gallium(III) and indium(III) and their properties. Obtain $Ga(OH)_3[In(OH)_3]$ by an exchange reaction

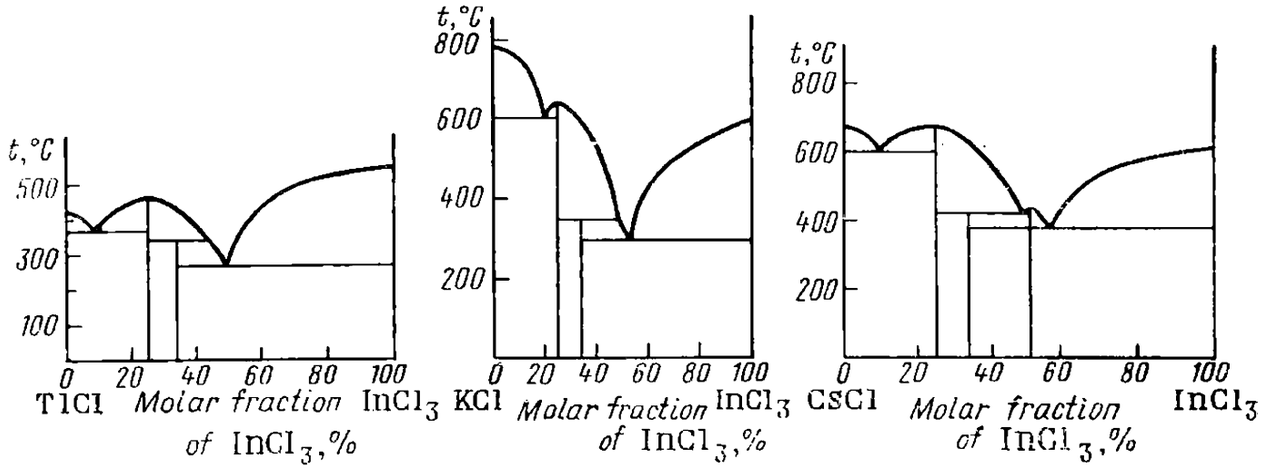


Fig. 57. Phase diagrams of the system $MCl\text{-}InCl_3$

between solutions of $GaCl_3[InCl_3]$ and ammonia and try its attitude to solutions of acid and alkali.

37. Calculate ΔG°_{298} of the reaction between $InCl_3$ and In; $TlCl_3$ and Tl.

(a) What are the stable oxidation states of indium and thallium?

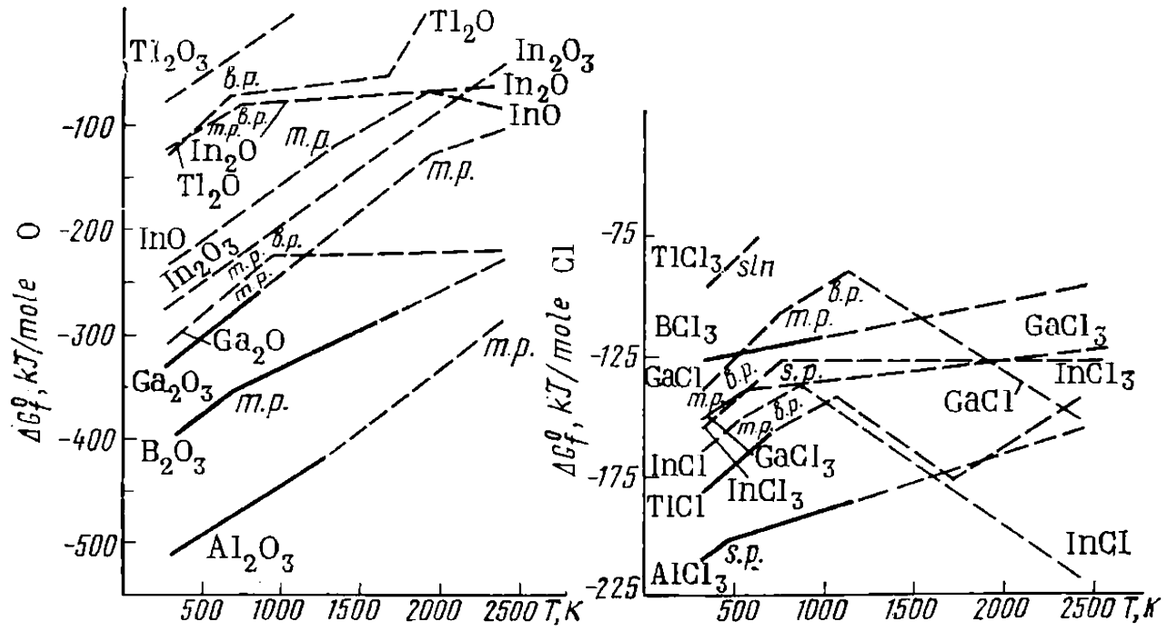


Fig. 58. Variation of ΔG°_f of some oxides and chlorides with temperature (for the legend see Fig. 21)

(b) What oxides and chlorides of gallium, indium and thallium are predominantly formed in reactions between the simple substances (Fig. 58)? Explain this fact.

(c) Explain the decreasing characteristic oxidation state in the series Ga-In-Tl.

(d) Characterize the oxidation-reduction properties of compounds of gallium, indium and thallium.

Experiment 28. Obtaining thallium(III) compounds. (Use the hood!) Add concentrated hydrochloric acid to a thallium(I) salt solution. Pass chlorine into the solution to dissolve the precipitate. Place the solution into a dish, evaporate to crystallization and use in the next experiment. Explain your observations.

Experiment 29. Oxidation-reduction properties of thallium(III) compounds. Add $SnCl_2$ solution to $TlCl_3$ solution. Explain your observations.

38. Compare ΔG°_{298} of reactions of Tl_2O and Tl_2O_3 with water (with reference to one mole of $H_2O(l)$). How do the acid-base properties of the oxides and hydroxides change with increasing oxidation state of thallium?

Experiment 30. Comparing the chemical nature and solubility of hydroxides of thallium(I) and thallium(III). Add an alkali solution to solutions of nitrates of thallium(I) and thallium(III). In which case does a precipitate fall out? Determine its chemical nature.

39. Describe the structure of BN (borazon), AlP, GaAs, InSb and answer the following questions.

(a) Why are the internuclear distances and the bond energies similar in the following pairs: C (diamond)-BN (borazon), Si-AlP, Ge-GaAs, α-Sn-InSb?

(b) How do the forbidden zone width, melting point and hardness change in the series BN-AlP-GaAs-InSb? Explain.

(c) What is the practical importance of the $A^{III}B^{V}$ type compounds of the elements of the gallium subgroup?

CHAPTER 6

s-Elements of Group II

6.1. Elements and Simple Substances

1. Construct graphs showing the variation of the ionization potentials (I_1, I_2, I_3), atomic and ionic radii of the *s*-elements of group II with their atomic number.

(a) Explain the curves.

(b) What neighbour-elements in the series Be-Mg-Ca-Sr-Ba have the most similar and most dissimilar properties?

2. Figure 59 shows the variation of ΔG_f of some oxides, fluorides, chlorides and nitrides with temperature.

(a) How does the chemical activity in the series Be-Mg-Ca-Sr-Ba change in their reactions with oxygen, fluorine, chlorine and nitrogen?

(b) What conditions are required to obtain the metals by chemical reduction of their oxides? Is this process profitable?

(c) What methods of obtaining said metals are used in industry?

3. Compare the standard electrode potentials of the metals of the *s*-elements of group II.

(a) Explain the character of variation of the potentials in the subgroup from the point of view of the enthalpy cycle

$$\begin{array}{ccc} M(c) & \xrightarrow{\Delta H_{subl}} & M(g) \\ \downarrow \Delta H_f & & \downarrow \Delta H_{ion} \\ M^{2+}(sln) & \xleftarrow[\Delta H_{hydr}]{} & M^{2+}(g) + 2e^- \end{array}$$

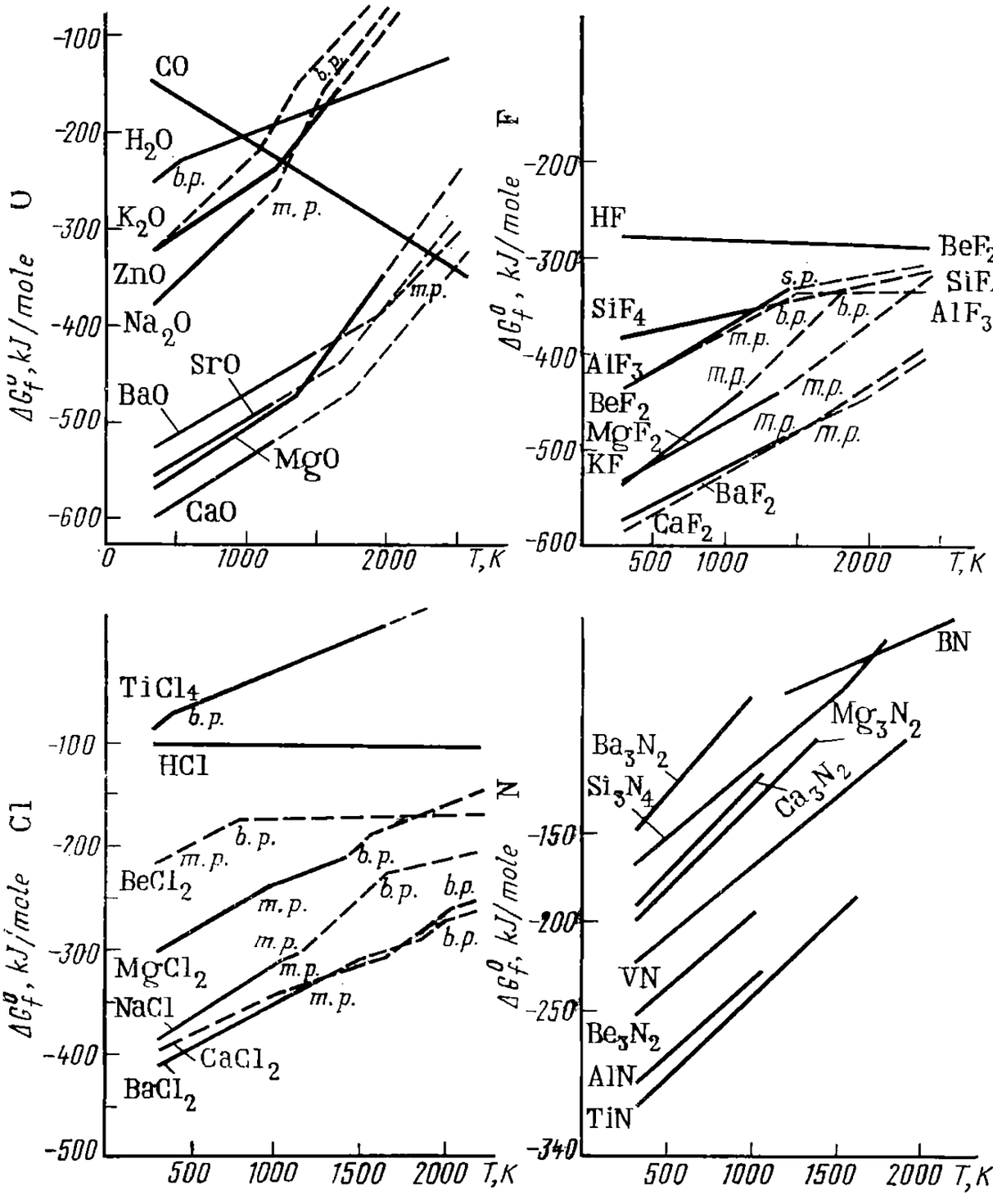


Fig. 59. Variation of ΔG_f of some oxides, fluorides, chlorides and nitrides with temperature (for the legend see Fig. 21)

(b) E°_{298} of beryllium and magnesium are negative values but the metals are insoluble in water. Why?

Experiment 1. Reaction of magnesium with water in the cold and with heating. Try the attitude of magnesium to water in the cold and with heating. Determine the reaction (pH) of the solutions obtained (first cool the hot solution) and explain the results of the experiment.

Experiment 2. Reaction of calcium with water. Try the attitude of calcium to water.

4. Calculate ΔH°_{298}, ΔS°_{298} and ΔG°_{298} of oxidation (by oxygen) of calcium and barium oxides to their peroxides.

(a) How does temperature affect the equilibrium of these reactions? Explain.

(b) Combustion of what metal, calcium or barium, is more likely to give the peroxide?

Experiment 3. Combustion of calcium (barium) in air. Take a piece of calcium (barium) with a forceps and burn it over a dry porcelain dish. Dissolve the obtained product in water and decide if the solution contains calcium (barium) peroxide.

6.2. Compounds of *s*-Elements of Group II

5. Calculate the temperature of thermal decomposition of $BaCO_3$ and $Ba(NO_3)_2$ at which the partial pressure of gases is 101.325 kPa.

Which of the compounds, $BaCO_3$ or $Ba(NO_3)_2$, is used in laboratory to obtain BaO?

Experiment 4. Obtaining barium oxide by decomposing salt. Place carbonate and nitrate of barium into two separate test tubes provided with gas outlet tubes. Fix them in a stand and heat over a burner. Pass the gaseous products into a beaker containing an alkali solution and observe in which test tube the gas evolves earlier. Explain your observations.

6. Construct a graph showing the variation of ΔG°_{298} of the formation of the oxides ECO_3, $E(OH)_2$, ESO_4 and $ESiO_3$ with the atomic number of *s*-elements of group II.

(a) Arrange the oxides (1) in the order of their increasing basic properties, and (2) in the order of increasing acid properties of other oxides formed along with the oxides of the *s*-elements.

(b) Calculate the temperature of decomposition of $MgCO_3$, $CaCO_3$, and $BaCO_3$ at which the pressure of CO_2 is 101.325 kPa.

(c) Explain the increasing thermal stability of MCO_3, $MSiO_3$ and MSO_4 with the increasing atomic number of the *s*-elements.

Experiment 5. Comparing thermal stability of carbonates. Place carbonates of magnesium, calcium and barium into separate test tubes provided with gas outlet tubes. Fix them in a stand and heat over a burner. Pass the gaseous products into beakers containing $Ca(OH)_2$ solution. Explain the succession in which the solutions in the beakers become cloudy.

Experiment 6. Comparing chemical activity of oxides and solubility of hydroxides of *s*-elements of group II. (a) Wet oxides of magnesium, calcium and barium in dry crucibles with 2-3 drops of water. Where is the reaction more energetic?

(b) Add an equal volume of sodium hydroxide solution to equimolar solutions of salts of calcium, strontium and barium in separate test tubes. The bulks of the precipitates in the test tubes are different. Explain.

7. The valency oscillation frequencies (ν) of the Be—F bonds in beryllium difluoride and of the C—O bond in carbon dioxide in the gaseous and the crystal states are as follows:

	BeF_2 (g)	BeF_2 (c)	CO_2 (g)	CO_2 (c)
$\tilde{\nu}$, cm^{-1} . .	1555	760	2349	2344

Why, in contrast to CO_2, does the valency oscillation frequency of BeF_2 sharply change in the transition from the gaseous state to the crystal state?

8. How does the structure of BeF_2 differ from that of $BeCl_2$ and what effect it has on their properties?

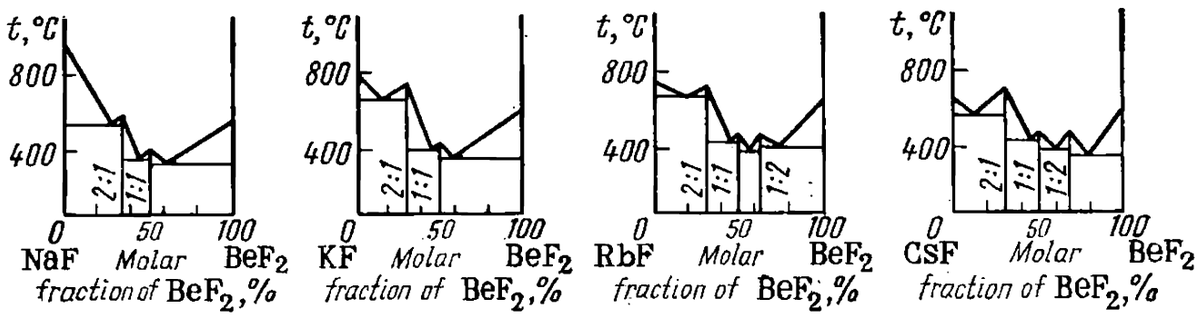


Fig. 60. Simplified phase diagram of the system MF-BeF_2

9. Figure 60 shows the phase diagrams of some systems.

(a) What compounds are formed in said systems and how does the stability of the compounds depend on the nature of the *s*-elements of group I?

(b) How do the acid-base properties of similar dihalides change in the series Be(II)-Mg(II)-Ca(II)-Sr(II)-Ba(II)?

10. Explain the structure of the ions $[Be(H_2O)_4]^{2+}$ and $[Mg(H_2O)_6]^{2+}$.

(a) Explain the decreasing force constant of the M—OH_2 bond in the transition from $Be(OH_2)_4^{2+}$ (295 N/m) to $Mg(OH_2)_6^{2+}$ (115 N/m).

(b) What effect it has on the comparative degree of hydrolysis of salts with respect to the cation Be^{2+} and Mg^{2+}?

(c) Give the equation of hydrolysis of $BeCl_2$.

(d) Can BeS be obtained by an exchange reaction in an aqueous solution?

11. Give examples of reactions to illustrate the amphoteric character of Be, BeO and $Be(OH)_2$.

12. Compare the solubility of salts of Ca(II), Sr(II) and Ba(II) in water (Fig. 61).

(a) What salts of Ca(II), Sr(II) and Ba(II) are the least soluble in water?

(b) The presence of what salts accounts for temporary and permanent hardness of water?

What reaction is responsible for deposition of scale during boiling natural water in a kettle?

(c) How can temporary and permanent hardness of water be removed?

Experiment 7. Comparing solubility of calcium carbonate and calcium hydrocarbonate. Pass carbon dioxide gas into a strongly dilute lime water. Explain precipitation of a substance and its subsequent dissolution during the continuing passage of carbon dioxide through the solution. Separate the carbonate precipitate by two different methods. Explain your observations.

13. Explain the principle underlying the method of removal of water hardness by ion exchange.

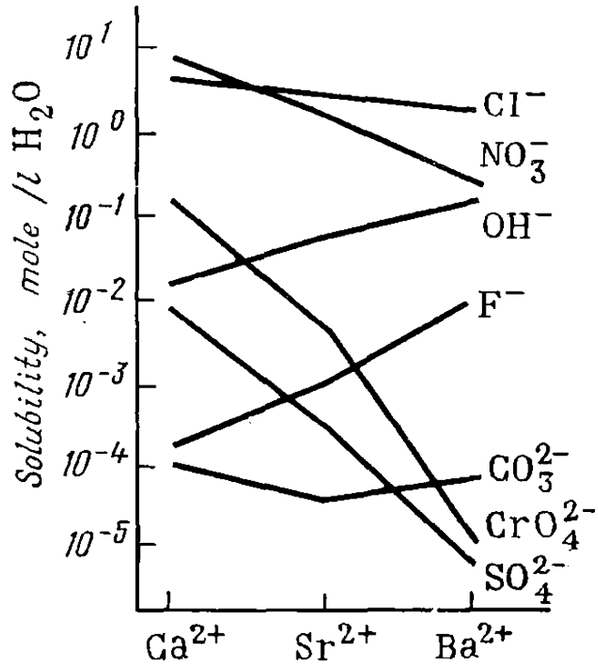


Fig. 61. Solubility of calcium, strontium and barium salts in water

Experiment 8. Removal of water hardness by ion exchange. Pack a column with cation-exchange resin and pass slowly (by drops) a strongly diluted solution of any calcium salt. Test the effluent solution for the calcium ion.

Pass slowly, also by drops, a strongly diluted solution of sodium sulphate through a column packed with anion-exchange resin. Test the treated solution for the sulphate ion.

CHAPTER 7
s-Elements of Group I

7.1. Elements and Simple Substances

1. Show graphically the variation of ionization potentials (I_1, I_2, I_3) and atomic and ionic radii with the atomic number.

(a) Explain the curves.

(b) What neighbour-elements in the series Li-Na-K-Rb-Cs-Fr have the greatest and the least similarity?

(c) Explain the stability of the oxidation state of *s*-elements in Group I.

2. How do the melting and boiling points vary in the series of the alkali metals? Explain.

3. Explain the difference between the phase diagrams shown in Fig. 62.

Experiment 1. Acquaintance with liquid alloy of sodium and potassium. Compare the state of aggregation and the appearance of sodium, potassium and liquid alloy of these metals sealed in ampoules. Using the phase diagram (Fig. 62*b*) indicate the composition of the Na-K alloy which is liquid in normal conditions. What compounds are formed in this system?

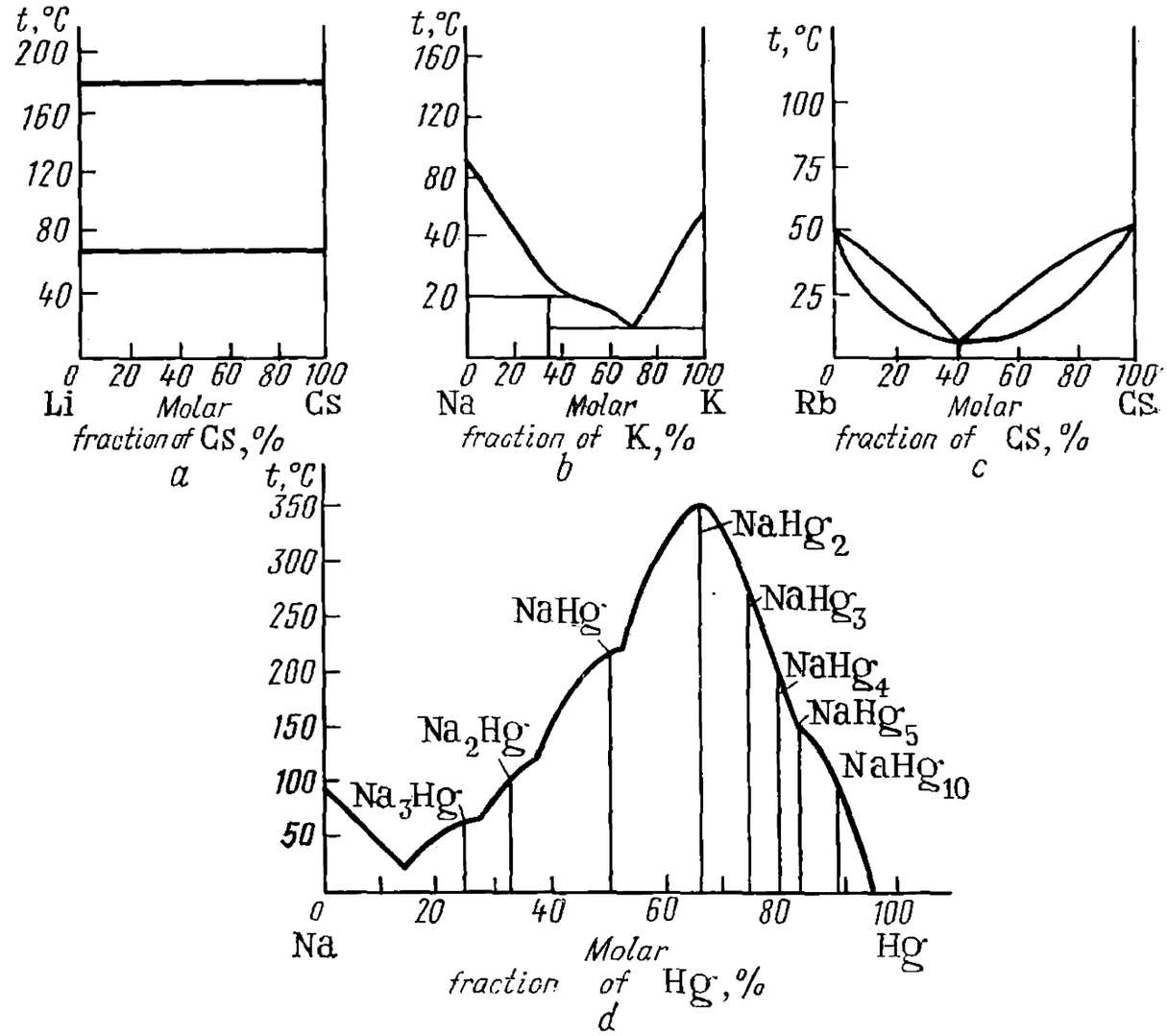


Fig. 62. Phase diagrams of the system Li-Cs (*a*), Na-K (*b*), Rb-Cs (*c*) and Na-Hg (*d*)

4. (a) Give the formula of the most stable compound which is present in sodium amalgam (Fig. 62*d*).

(b) What is the practical value of sodium amalgam?

Experiment 2. Obtaining sodium amalgam. (Use the hood. Lower the protective screen!) Place a small amount of mercury into a dry porcelain mortar and add a small grain of sodium metal. Grind carefully the sodium by a pestle. The reaction of sodium with mer-

cury produces a flash. The amalgam can be liquid or solid, depending on the temperature and on the mercury to sodium ratio. Keep the amalgam obtained for next experiments.

5. What oxygen compounds are formed by burning the alkali metals?

Experiment 3. The attitude of the alkali metals to air in the cold and with heating. (Use the hood!) Using forceps, remove a piece of sodium (potassium) metal from a bottle filled with kerosine. Place the metal on a sheet of filter paper and cut a small piece, not bigger than the size of a pea. (NEVER touch the metal with your hands!) Explain why the fresh section of the metal quickly dulls on exposure to air. Place the separated slice on the crucible lid and heat from underneath. When the metal melts, light it from a burner and quickly drop the protective screen of the hood. When the metal is all burnt, cool the product of combustion and dissolve in 2-3 ml of distilled water. (Be careful during the dissolution because unburnt residues may be contained in the material!)

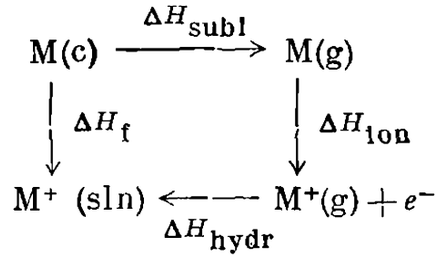
Add potassium iodide solution acidified with sulphuric acid and 2-3 drops of starch solution. Draw your conclusions concerning the character of the products of sodium (potassium) combustion.

Repeat the experiment, taking lithium instead of sodium or potassium. What products are formed by oxidation of lithium?

6. Show graphically the variation of ΔH_{subl} of the metal, ΔH_{hydr} of the ion M^+, and ΔH_{ion} of the atom with the atomic number of *s*-element in Group I.

(a) Explain the curves.

(b) Explain the character of variation of the standard electrode potential of the alkali metals with their increasing atomic number using the enthalpy diagram.



Experiment 4. Comparing the chemical activity of the alkali metals. Using forceps drop a piece of sodium into a crystallization dish containing water and phenolphthalein. Cover the dish with a glass. Observe the reaction. Act similarly with lithium and potassium. Compare the chemical activities of the alkali metals in reaction with water.

Experiment 5. Reducing properties of sodium amalgam. Add carefully, by small portions, part of the obtained sodium amalgam into an acidified potassium permanganate solution. (Half close the hood!) Write the equation of the reaction (assume the composition of the amalgam to be $NaHg_2$).

7. Draw a graph showing the variation of ΔH_f° of hydrides, iodides and fluorides with the atomic number of *s*-elements of Group I. Explain the curves. The analysis of the Born-Haber cycles can be used in the answer.

7.2. Compounds of *s*-Elements of Group I

8. Figure 63 shows phase diagrams of several systems.

(a) Explain the different characters of the diagrams.

(b) What is the practical importance of the $CaCl_2$ and KCl addition in obtaining sodium or lithium by electrolysis of molten NaCl or LiCl respectively?

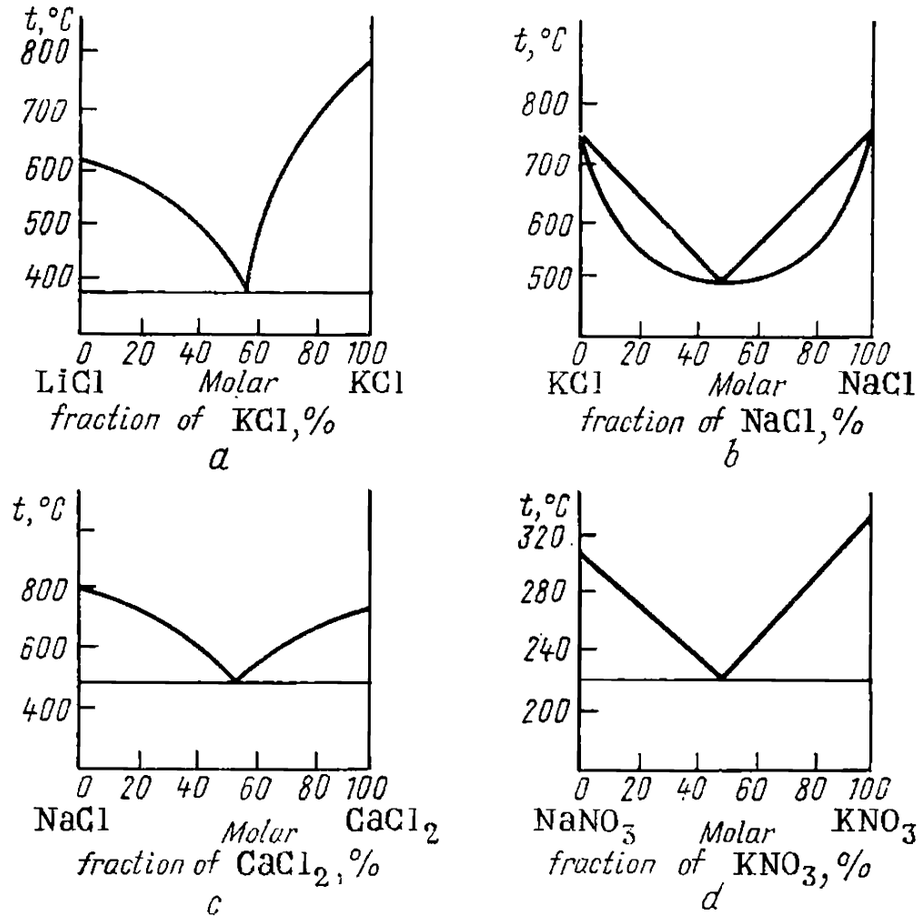


Fig. 63. Phase diagrams of the systems LiCl-KCl (*a*), KCl-NaCl (*b*), NaCl-$CaCl_2$ (*c*) and $NaNO_3$-KNO_3

9. Construct and explain a graph showing the variation of ΔG°_{298} of formation of EOH(c), E_2CO_3(c) and E_2SO_4(c) from the oxides with the atomic number of *s*-elements of group I.

10. What compounds are formed in the following systems: NaCl-$AlCl_3$, KCl-$AlCl_3$, RbCl-$AlCl_3$, CsCl-$AlCl_3$ and how does their stability change in the series Na^+-K^+-Rb^+-Cs^+? Explain the revealed regularity.

11. Describe the industrial methods of obtaining alkalis.

(a) An electrolysis of an aqueous solution of NaCl gave 70 l of

a 10.6 per cent solution of NaOH (density, 1.12 g/cc). What quantity of NaCl was converted into NaOH?

(b) Into what direction and why is the equilibrium displaced during the reaction of potassium carbonate with calcium hydroxide in an aqueous solution?

Experiment 6. Obtaining sodium hydroxide by electrolysis of sodium chloride solution. Electrolize a solution of NaCl in an electrolytic cell with a porous diaphragm. Identify experimentally the gas that evolves at the anode and determine the reaction (pH) of the medium at the cathode.

Experiment 7. Obtaining sodium hydroxide by the reaction of amalgam with water. Add sodium amalgam, by small portions, to water. (Half close the hood!) When the reaction is over, make sure that alkali has formed in solution.

12. It has been shown experimentally that Rb_2O_2 and RbO_2 (in the molten eutectic $LiNO_3$-KNO_3) are ionized as follows:

$$Rb_2O_2 \rightleftarrows 2Rb^+ + O_2^{2-}; \quad RbO_2 \rightleftarrows Rb^+ + O_2$$

(a) What type of compounds are Rb_2O_2 and RbO_2?

(b) Why are their properties studied in anhydrous solvents?

13. Write the equation for the reaction of obtaining soda from sodium sulphate by sintering the latter with coal and lime at high temperature. What functions do coal and limestone perform in this reaction?

14. Calculate the requirements for raw materials, viz., the volume of brine containing 300 g of NaCl in 1 litre of H_3N and CO_2 (in cubic metres at 0°C and 93.3 kPa) for the production of one ton of soda ash, assuming that only 2/3 sodium chloride is converted into soda, while carbon dioxide which is formed during calcining of sodium hydrocarbonate is all returned into the process.

Experiment 8. Obtaining sodium hydrocarbonate. Mix saturated solutions of sodium chloride and ammonium carbonate in a beaker and pass carbon dioxide into the solution until a precipitate falls out. Separate the precipitate and dry. Dissolve a small quantity of the obtained salt in water and try the solution with litmus, phenolphthalein and methyl orange. Explain your observations.

Experiment 9. Obtaining sodium carbonate. Calcine sodium bicarbonate obtained in Experiment 8 in a porcelain crucible until water vapour stops evolving. Cool the product, dissolve in water and try the solution with acid-base indicators. Give your explanations.

Compare the character of hydrolysis of hydrocarbonate and carbonate of sodium.

15. Figure 64 shows the variation of solubility of NaCl and KCl in water with temperature.

(a) What methods of separation of NaCl and KCl are used in industry?

(b) What compounds of lithium, sodium and the elements of the

potassium subgroup are sparingly soluble?

(c) The interaction of 1 g of a mixture of KCl and NaCl with $H_2[PtCl_6]$ solution gives 1.5 g of sparingly soluble $K_2[PtCl_6]$. Calculate the percentage of KCl in the mixture.

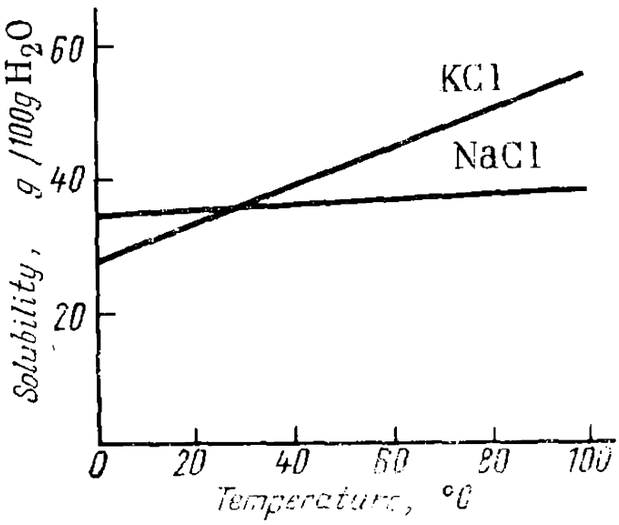


Fig. 64. Variation of solubility of NaCl and KCl in water with temperature

(d) A solution containing 40 g of KCl in 100 ml of water is added to a solution containing 70 g of $NaClO_4$ in 100 ml of water at 20°C. What substance and in what quantity is precipitated from the solution?

Experiment 10. Obtaining sparingly soluble compounds of potassium and sodium. (Qualitative tests for the alkali metal ions.) (a) Add solution of potassium hexahydroxystibate(V) to an equal volume of a neutral solution of a sodium salt. Cool the test tube with tap water and, using a glass rod, rub carefully inside the walls of the test tube: white fine crystals of sodium hexahydroxystibate precipitate. Explain why?

(b) The interaction of solutions of a potassium salt and sodium perchlorate gives a precipitate. Explain.

(c) Add a solution of sodium hexanitrite cobaltate(III) to a potassium salt solution acidified with acetic acid. Explain precipitation of a yellow substance.

16. The solubilities of perchlorates in water, ethanol, and acetone (1 g in 100 g of solution at 25°C) are tabulated below:

	$LiClO_4$	$NaClO_4$	$KClO_4$
H_2O	27	68	1.3
C_2H_5OH	60	13	0.01
$(CH_3)_2CO$	58	34	0.16

Unlike salts of the other alkali metals, the salts of lithium are well soluble in polar organic solvents. Explain.

17. The highest intensity of lines in the visible region of the emission spectrum of lithium and sodium is at 670.8 and 584.3 nm respectively.

(a) What is the colour of the flame of lithium and sodium compounds?

(b) What is the practical importance of the ability of compounds to colour flame?

Experiment 11. Flame coloration by salts of alkali and alkaline-earth metals. (Flame Test.) Using a platinum wire, introduce into a nonluminous flame compounds of the alkali and alkaline-earth metals, one after another. Note the colour of the flame.

II

d-ELEMENTS OF THE MENDELEEV PERIODIC SYSTEM

CHAPTER 8

General Properties of the *d*-Elements

8.1. Introduction

1. Give electron configuration of the elements in the series Sc-Zn.

(a) What orbitals and electrons of the *d*-elements are valent ones? Explain.

(b) Why are the *d*-elements characterized by a variety of oxidation states? How does the highest oxidation state change in the series Sc-Zn?

2. Construct a graph showing the variation of the first (I_1), the second (I_2) and the third (I_3) ionization potentials with the atomic number of elements in the series Ca-Ga.

(a) Explain the general tendency of the first ionization potential to increase with the atomic number of the element. Why does the monotonous variation of the I_1 values change markedly in the transition from Cr to Mn and from Cu to Zn?

(b) The I_2 value of what elements differs markedly from that of the neighbouring elements? What is the electron configuration of their unicharged ions?

(c) The I_3 value of what elements differs markedly from that of the neighbouring elements? What is the electron configuration of their doubly charged ions?

(d) Explain the characteristic maxima of each curve.

3. What is the electron configuration of ions of elements of the following oxidation states: Cr(III), Cr(VI), Mn(II), Mn(IV), Mn(VII), Fe(II), Fe(III), Cu(I), Cu(II), Cu(III), Zn(II), Hg(II), Sc(III), Ti(IV)?

8.2. Complex Compounds

4. Examples of complex compounds of *d*-elements are given below: $K_2[Zn(OH)_4]$, $[Zn(OH_2)_4]Cl_2$, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_6]Cl_4$, $[Cr(NH_3)_3(OH_2)_3]Cl_3$, $K_3[Co(NO_2)_6]$.

(a) Determine the complex charge, the oxidation state and the coordination number of the complexing agent.

(b) What compounds contain cation complexes and what anion complexes? What complexes are electrically neutral?

(c) Give names of complex compounds.

5. Qualitative reactions for constituent ions and molecules are used for the determination of the composition of the inner and outer

spheres of complex compounds. If the complex is sufficiently stable, its constituent parts are incapable of reactions characteristic of them in the free state in solution. At the same time, the ions of the outer sphere of the complex compound are free in solution and are easily detectable by qualitative tests.

Compounds of the following composition are known for cobalt(III): $CoCl_3 \cdot 6NH_3$, $CoCl_3 \cdot 5NH_3 \cdot H_2O$, $CoCl_3 \cdot 5NH_3$, $CoCl_3 \cdot 4NH_3$. The action of $AgNO_3$ solution on the solution of these compounds reveals the following: all chlorine is practically precipitated from solution of the former two compounds, only two thirds of all chlorine is precipitated from the third and one third from the fourth solution.

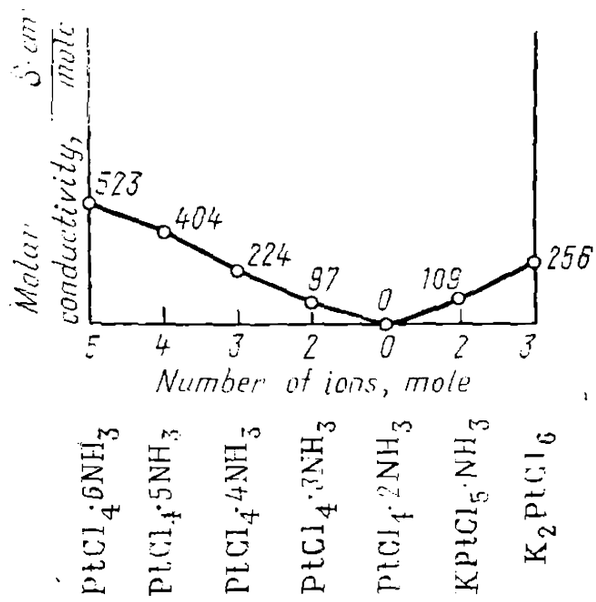


Fig. 65. Molar electrical conductivity of complex compounds of platinum(IV)

(a) What is the coordination number of the complexing agent and the structure of the compounds? Write the equation of their ionization.

(b) Name the complex compounds.

6. Measurement of molar conductivity of solutions is the most popular physico-chemical method of studying complex compounds. Electric conductivity of millimolar solutions is usually measured. If one mole of a compound falls into two moles of ions, the electric conductivity of such a solution is about 100 $S \cdot cm^2$/mole; if it falls into three moles of ions, the conductivity increases to 250 $S \cdot cm^2$/mole; if into 4 moles, about 400 $S \cdot cm^2$/mole, and if into 5 moles, about 500 $S \cdot cm^2$/mole.

Figure 65 shows the results of measurement of electrical conductivity of platinum(IV) compounds.

(a) What is the coordination structure of the compounds? Write equations for their ionization.

(b) Name the complex compounds.

8.3. Description of Complexes from the Standpoint of the Valence Bond Theory (VB)

7. Formulate the main principles of the valence bond theory to explain the formation and the structure of complex compounds.

(a) Explain the tendency of *d*-elements to form complex compounds.

(b) Using values of energy of hydration of the cations Ca^{2+}, Ti^{2+}, V^{2+}, Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, characterize the ability of the ions to the donor-acceptor interaction with water molecules depending on their charge and the cation size.

8. Following below are examples of diamagnetic complexes:

I. $[Cu(NH_3)_2]^+$, $[AgBr_2]^-$, $[Au(CN)_2]^-$

II. $[Zn(NH_3)_4]^{2+}$, $[Zn(OH)_4]^{2-}$, $[Hg(CN)_4]^{2-}$

III. $[Pt(NH_3)_4]^{2+}$, $[Pt(NH_3)_2Cl_2]^0$, $[PdCl_4]^{2-}$

IV. $[AuCl_4]^-$, $[AuBr_4]^-$

V. $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)_6]^{3-}$

VI. $[Pt(NH_3)_6]^{4+}$, $[Pt(NH_3)_2Cl_4]^0$, $[PtCl_6]^{2-}$

(a) Determine the oxidation state and the electron configuration of complexing agents.

(b) What type of hybridization can be attributed to the orbitals of the central atom (c.a.) involved in the formation of bonds and what is the spatial configuration of the complexes in this series?

(c) Tabulate the data obtained.

Oxidation state of c.a.	Electron configuration of c.a.	Coordination number of c.a.	Orbital hybridization of c.a.	Spatial configuration of complex	Examples of compounds

(d) What spatial configurations of complexes can correspond to diamagnetic ions with the configuration d^{10}, d^8, d^6?

9. Write the formulas of complex ions of chromium(III) if its coordination number is 6 and the molecules of H_2O, H_3N and the ions F^-, OH^- are their ligands? Name the complexes.

(a) Write equations of reactions of amphoteric chromium(III) hydroxide with acids and alkalis (assume the formation of Cr(III) complex ions). The presence of what ions promote the formation of cation aqua complexes, anion hydroxy complexes?

(b) Using the VB method describe the structure of these complexes if each of them contains three unpaired electrons.

Experiment 1. Formation of cation aqua complexes and anion hydroxy complexes of chromium(III). Obtain chromium(III) hydroxide and examine its acid-base properties. Explain your observations.

10. By what reactions can amphoteric zinc(II) hydroxide be transformed into aqua and hydroxy complexes of Zn(II)?

Describe their structure if the coordination number of Zn(II) is 4.

Experiment 2. Formation of cation aqua complexes and anion hydroxy complexes of zinc(II). Obtain zinc hydroxide and examine its acid-base properties. Explain your observations.

11. Explain the structure of ammine complexes of Zn(II) and Ag(I), if their coordination numbers are 4 and 2 respectively. What reaction shall be used to obtain ammoniates?

Experiment 3. Formation of ammine complexes of Zn(II) and Ag(I). Add, by drops, ammonia solution to solutions of salts of Zn(II) and Ag(I). Explain the formation of precipitates and their dissolution in excess ammonia solution. Compare the attitude of the solutions obtained and the solutions of Zn(II) and Ag(I) salts to alkali. Give your explanations.

12. Describe the formation and the structure of the iodide complex of mercury(II) if its coordination number is 4. Name the complex. What reaction can be used to obtain the complex?

Experiment 4. Formation of tetraiodomercuriate(II) complex. Add concentrated KI solution, by drops, to $Hg(NO_3)_2$ solution. Explain your observations. Check to see if a precipitate is formed in the reaction of the solution obtained with alkali. Try the action of alkali on $Hg(NO_3)_2$. Compare the results and give your explanations.

13. Write the equation of the reaction by which the $[AgCl_2]^-$ ion is formed and describe its structure. Name the complex.

Experiment 5. Formation of dichlorargentate(I) complex. Obtain silver chloride by an exchange reaction between silver nitrate and sodium chloride. Act with saturated sodium chloride solution on the precipitate. Explain your observations.

Compare the attitude of the obtained solution and silver nitrate solution to alkali.

8.4. Description of Complexes from the Standpoint of the Crystal-Field Theory

14. Formulate the main principles of the crystal-field theory.

(a) Why and how is the degeneration of 3*d*-orbitals removed in the octahedral and tetrahedral ligand field?

(b) Draw the diagrams of energy levels and show the distribution of electrons in *d*-orbitals of ion-complexing agent in the following cases: d^4, octahedral field, low-spin complex; d^6, tetrahedral field, high-spin complex; d^7, octahedral field, high-spin complex.

15. Give the energy of splitting of *d*-level of nickel(II) in its octahedral complexes: $[Ni(OH_2)_6]^{2+}$, $[Ni(NH_3)_6[^{2+}$, $[NiF_6]^{4-}$, $[NiCl_6]^{4-}$, $[NiBr_6]^{4-}$.

Arrange the ligands in the order of their increasing power to split *d*-orbitals and compare the series formed with the spectrochemical series of ligands.

16. Give the energy of splitting of the *d*-level of the Co^{3+} ion in the $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ complexes and the energy of pairing of *d*-electrons (the energy of the interelectron repulsion) in the Co^{3+} ion.

(a) Distribute *d*-electrons in the orbitals of Co^{3+} in the octahedral field of F^- ions and H_3N molecules.

(b) Are these complexes high-spin or low-spin, para- or diamagnetic? Explain the different properties of the complexes.

17. Construct graphs showing the variation of the radius and the enthalpy of hydration in the series Ca^{2+}-Zn^{2+}. Explain the curves from distributing the electrons in d_ε- and d_γ-orbitals of ions in the series Ca^{2+}-Zn^{2+}, in the octahedral environment of a weak field.

18. Explain the variation of the energy of crystal lattice of dichlorides in the series Ca^{2+}-Zn^{2+} (solid curve, Fig. 66).

19. (a) Explain the increasing energy of splitting of *d*-level in the series of similar complexes 3*d*-, 4*d*- and 5*d*-elements, for example: $Co(NH_3)_6^{3+}$ (273 kJ/mole)-$Rh(NH_3)_6^{3+}$ (407 kJ/mole)-$Ir(NH_3)_6^{3+}$ (477 kJ/mole).

(b) Give Δ of the ions $Co(NH_3)_6^{2+}$ and $Co(NH_3)_6^{3+}$. Explain the difference.

20. Construct the energy diagram of the Ti^{3+} ion orbitals in the $Ti(OH_2)_6^{3+}$ complex.

(a) To what orbital can the electron be transferred?

(b) What is the colour of the $Ti(OH_2)_6^{3+}$ ion, if the electron transfer corresponds to absorption of energy $\Delta = 2.48$ eV? Calculate the wavelength of the absorbed light and determine the colour of the complex.

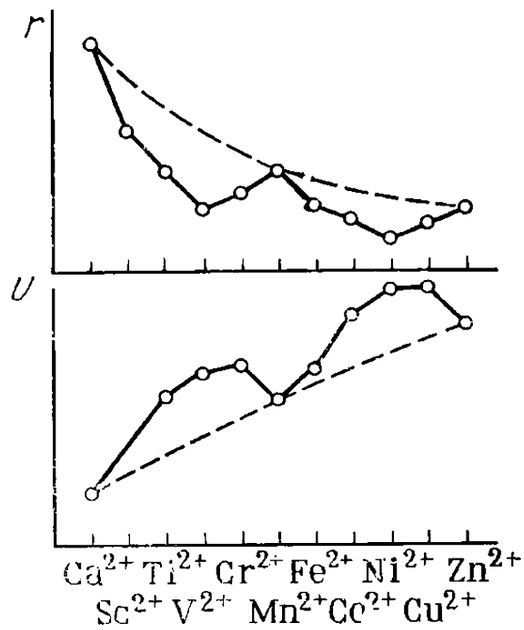


Fig. 66. Variation of crystal lattice energy of dichlorides in the series Ca^{2+}-Zn^{2+}

(c) Why are compounds of the Ca^{2+} and Zn^{2+} ions colourless?

Experiment 6. Effect of electron configuration of complexing agent on complex colour. Place a zinc granule into a strongly acid solution of titanium(IV) compound. Explain the colour change in the solution (assume that the compound of titanium(IV) converts into the compound of titanium(III)).

21. The colours of anhydrous copper(II) sulphate, blue vitriol and copper(II) ammoniate are different. Explain why.

Experiment 7. Effect of ligand nature on complex colour. Dissolve anhydrous copper(II) sulphate in water. Add ammonia solution. Explain your observations.

Experiment 8. Comparing the colour of anhydrous salts and crystal hydrates. Heat crystal hydrates $CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$,

$CrCl_3 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$ in a crucible and obtain the anhydrous salts. Cool them and add water. Explain why the colour of the substances changes on heating and dissolution.

8.5. Description of Complexes from the Standpoint of the Molecular Orbital (MO) Theory

22. Formulate the main principles of the molecular orbital theory as applied to the description of complex compounds.

(a) Give schemes of overlapping of *s*-, *p*-, *d*-orbitals of the central atom and group orbitals of ligands for an octahedral complex without π-bonding.

(b) Construct an approximate energy diagram of molecular orbitals in an octahedral complex.

23. Distribute valency electrons in orbitals and determine the electron configuration of the octahedral complexes $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$, using the data of Problem 16.

(a) Electrons of what molecular orbitals account for bonding in these complexes?

(b) Which of these complexes is para- and diamagnetic, low-spin and high-spin? Explain.

(c) Compare the descriptions of a diamagnetic complex from the standpoints of the MO theory, the VB theory and of the CF theory.

24. Draw a diagram of molecular orbitals for the $Ag(NH_3)_2^+$ complex ion having the linear structure. Compare the descriptions of the complex from the standpoints of the MO and VB theories (Problem 11).

25. Draw types of π-overlapping of π_d-orbitals of the central atom of an octahedral complex with suitable (by symmetry) group orbitals of the ligands.

(a) What is the main difference between the π-donor-acceptor and π-dative interaction?

(b) How does the value of Δ of the complex depend on the probability of the π-donor-acceptor and dative interaction between the complexing agent and the ligands?

(c) Explain from this standpoint the order of ligand arrangement in the spectrochemical series.

26. It has been shown experimentally that the $[Co(CN)_6]^{3-}$ octahedral complex is diamagnetic.

(a) What types of donor-acceptor interaction are possible between the Co^{3+} and CN^- ions if the latter can be both σ-donor and π-acceptor (the presence of free π* molecular orbitals)?

(b) Explain the order of the Co—CN bond. Why is the $[Co(CN)_6]^{3-}$ complex especially stable?

8.6. Chemical Equilibrium in Solutions Containing Complex Compounds

27. Write the equations of ionization of $[Cd(NH_3)_4]Cl_2$ and $K_2[Cd(CN)_4]$ in solution and equations of ionization of complex ions formed in the reactions.

(a) Write the expressions of the general instability constant and the general stability constant of the complexes.

(b) Give the values of the general stability constant of the $[Cd(NH_3)_4]^{2+}$ and $[Cd(CN)_4]^{2-}$ ions. Which ion is more stable? Explain your answer.

28. Give the general stability constant of the $[Cu(NH_3)_4]^{2+}$ complex.

Calculate the variation of the Gibbs free energy in standard conditions at 25°C for the formation of this complex from Cu^{2+} ion and H_3N molecules.

29. Write the expression of general stability constants and give their values for silver(I) complexes given in Appendix 19.

(a) Which silver(I) complex is the most stable and which the least stable?

(b) Write equations for reactions by which said complexes are obtained from $AgNO_3$, and H_3N, $Na_2S_2O_3$, $NaNO_2$ and KCN solutions.

Experiment 9. Obtaining complexes and comparing their stability. Obtain the ammoniate, thiosulphate and nitrite complexes of Ag(I) in three separate test tubes. Add, by drops, sodium chloride solution to the obtained solutions of complex compounds. Add potassium bromide solution into two test tubes where no precipitate falls out. Add potassium iodide solution into the third test tube containing no precipitate.

Explain your observations. Mind the difference in the general stability constants of the complexes and the solubility products of silver halides.

Experiment 10. Dissolving precipitates due to complex formation. Place AgBr precipitate obtained by an exchange reaction into two test tubes. Add ammonia solution into one and sodium thiosulphate solution into the other test tube. Explain your observations.

30. Explain the following experimental fact. It is impossible to detect the presence of the Ag^+ ion in the $[Ag(CN)_2]^-$ solution by the halide ions, but Ag_2S precipitates from solution containing the $[Ag(CN)_2]^-$ complexes in the presence of the S^{2-} ion.

CHAPTER 9

d-Elements of Group IV

9.1. Elements and Simple Substances

1. Construct graphs shcwing the variation of radii of atoms and E^{4+} ions, and the ionization energy with the atomic number of the elements of the titanium subgroup. Explain the curves.

(a) Explain the similarity of the atomic and ionic radii of zirconium and hafnium. How does the character of changes in the properties in the series Ti-Zr-Hf depend on this similarity?

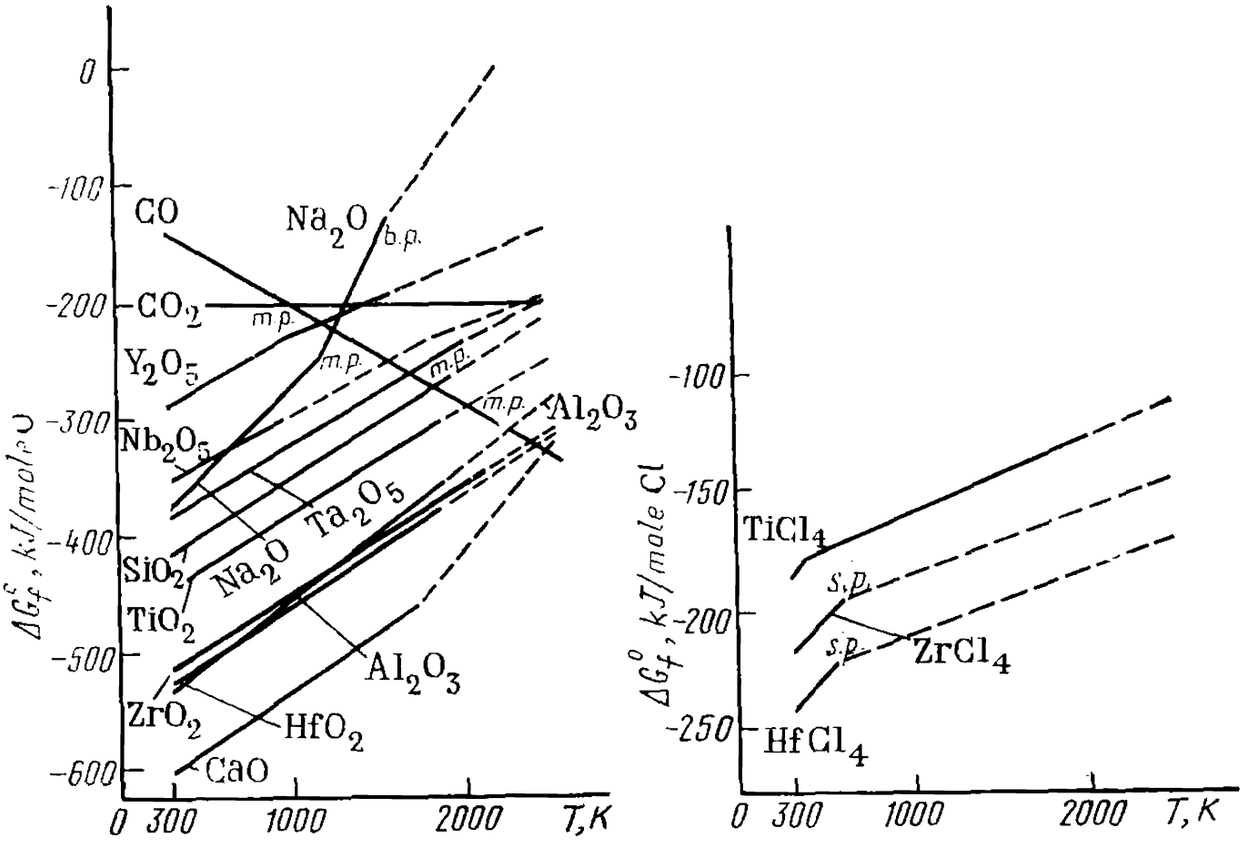


Fig. 67. Variation of ΔG_f° of some oxides and chlorides with temperature (for the legend see Fig. 21; *s. p.*—sublimation point)

(b) What are the oxidation states of Ti, Zr, Hf?

(c) How does the ability of the elements of the titanium subgroup to convert to higher oxidation state change with the increasing atomic number?

2. Describe the structure of titanium, zirconium and hafnium. Give T_{melt} and T_{boil}, ΔH_{melt} and ΔH_{subl} of the simple substances.

(a) How do the boiling and melting points, enthalpies of melting and sublimation of the simple substances change in subgroups of *d*-elements. Explain your answer.

(b) Characterize mechanical properties of metals and their importance in industry.

3. Figure 67 shows the variation of ΔG_f° of dioxides and tetrachlorides of titanium and its analogues with temperature.

(a) How does the chemical activity in reactions with oxygen and chlorine change in the series Ti-Zr-Hf?

(b) Titanium, zirconium and hafnium are corrosion-resistant in air in normal conditions. Explain why. What is the practical importance of this property of the metals?

9.2. Compounds of Ti(IV), Zr(IV) and Hf(IV)

4. (a) Can the hydrated ions Ti^{4+}, Zr^{4+}, Hf^{4+} exist in aqueous solutions?

(b) Write the equation of hydrolysis of $Ti(SO_4)_2$ assuming the formation of the titanyl TiO^{2+} derivatives (in the cold) and of titanium(IV) hydroxide (with heating).

5. Describe the structure of crystals of titanium dioxide and its analogues.

(a) What are the coordination numbers of Ti(IV), Zr(IV) and Hf(IV) in these compounds?

(b) What is the character of variation of the melting point, ΔH_f° and ΔG_f° in the series TiO_2-ZrO_2-HfO_2? Explain the similarity of the properties of ZrO_2 and HfO_2.

(c) What properties of titanium dioxide and its analogues account for their use in industry?

6. Characterize the acid-base properties of oxides and hydroxides of titanium(IV) and its analogues.

(a) Can salts of the $Ti(SO_4)_2$ and $Ti(NO_3)_4$ type be formed in reactions of $Ti(OH)_4$ and of TiO_2 with acids in aqueous solutions? If no, then why? What are the products of the reaction?

(b) Examine the acid-base properties of TiO_2 in its reaction with $K_2S_2O_7$ and K_2CO_3 on fusion.

Experiment 1. Obtaining titanium(IV) sulphate and its hydrolysis. (Use the hood!) Grind thoroughly TiO_2 and fuse it with five volumes of $K_2S_2O_7$ in a porcelain crucible. Heat carefully to prevent vigorous evolution of SO_3 formed. Dissolve one part of the fused material in dilute H_2SO_4, and treat the remaining portion with water with heating. Explain the dissolution of the melt in sulphuric acid and the formation of a precipitate in water.

Experiment 2. Obtaining potassium oxytitanate(IV) and its hydrolysis. Heat a stoichiometric mixture of TiO_2 and K_2CO_3 in a porcelain crucible in a muffle furnace at a temperature of 700-800°C until a clear dark-green melt is obtained. Immerse the hot crucible carefully into cold water. If the melt is not separated from the crucible walls, break the crucible. Grind the cooled melt and try its action to water. Explain your observations.

7. Calculate ΔG_{298}° of the formation of $CaTiO_3$(c) and H_2O(g) in the reaction of $Ca(OH)_2$(c) with TiO_2(c) and with $TiO(OH)_2$(c).

(a) How does the chemical activity change in the series TiO_2-$TiO(OH)_2$-$Ti(OH)_4$? Explain your answer.

(b) How does the reactivity of hydroxides change with time? Explain.

Experiment 3. Obtaining titanium(IV) hydroxide and studying its properties. Obtain titanium hydroxide from a solution of a titanium(IV) compound. Examine its attitude to dilute acids, dilute and concentrated alkali solutions.

Experiment 4. Ageing of precipitated titanium(IV) hydroxide and changes in its properties.

Obtain Ti(IV) hydroxide by an exchange reaction. Boil the mixture carefully. Cool the test tube, try the action of dilute acids on the precipitate. Compare your observations with the results of Experiment 3.

Experiment 5. Studying the properties of zirconium(IV) hydroxide. Obtain Zr(IV) hydroxide. Try the action of dilute acids and alkali solution on a sample of the precipitate. Heat the remaining precipitate carefully, then cool and try its solubility in dilute hydrochloric acid. Compare and explain the results of Experiments 3, 4 and 5.

8. Describe the structure of perovskite and ilmenite.

(a) The oxytitanates(IV) of *d*-elements having the structure of ilmenite ($MnTiO_3$, $CoTiO_3$, $NiTiO_3$) are mixed oxides. Explain why.

(b) What is the industrial use of oxytitanates(IV)?

9. Describe chemical bonding in $EHal_4$ molecules from the standpoint of the MO theory.

(a) What is the role of π-bonding in the stabilization of these molecules?

(b) Explain the character of variation of bond energy in the series of tetrahalide molecules:

	TiF_4	$TiCl_4$	$TiBr_4$	TiI_4
E_{Ti-Hal}, kJ/mole . .	585	429	367	296
	ZrF_4	$ZrCl_4$	$ZrBr_4$	ZrI_4
E_{Zr-Hal}, kJ/mole . .	650	489	422	347

(c) What is the character of variation of ΔH_f° and ΔG_f° in the series TiF_4(g)-$TiCl_4$(g)-$TiBr_4$(g)-TiI_4(g)? Explain your answer.

10. Calculate ΔH_{298}° and ΔS_{298}° of oxidation of crystalline titanium to TiI_4(g) with gaseous iodine.

Explain theoretically and describe the practical procedure for the iodine method of metal purification.

11. Write equations of reactions for obtaining EF_4 and ECl_4 from EO_2.

12. It has been established experimentally that the halide complexes of titanium(IV) and its analogues can be arranged in the following series in the order of their decreasing stability:

$$EF_6^{2-} \gg ECl_6^{2-} > EBr_6^{2-} > EI_6^{2-}$$

Hydrofluoric acid energetically dissolves titanium dioxide with liberation of much heat, while hydrochloric acid does not produce appreciable chemical action on the oxide. Explain why.

13. Figure 68 shows the phase diagram of the system KCl-$ZrCl_4$. What compound is formed in this system? Explain your answer.

Experiment 6. Obtaining hexachlorotitanate(IV)-ions. (Use the hood!) Add a few drops of concentrated $TiCl_4$ solution to a concentrated HCl solution cooled below 0°C (in a mixture of salt and snow). Pass dry hydrogen chloride through the solution. Explain the development of yellow-orange colour in the solution. Add NH_4Cl to the solution. Explain precipitation of a yellow substance.

14. Write a general equation of $TiCl_4$ hydrolysis. What effect have the increasing temperature and pH on the character of the hydrolysis products?

Experiment 7. Hydrolysis of titanium tetrachloride. (a) Open a bottle containing $TiCl_4$. Explain the formation of fog.

(b) Add water to a solution of $TiCl_4$ acidified with hydrochloric acid. Boil the solution. Explain your observations.

Experiment 8. Hydrolysis of zirconium tetrachloride. Place $ZrCl_4$ crystals into a porcelain dish. Explain the fume which appears in the air.

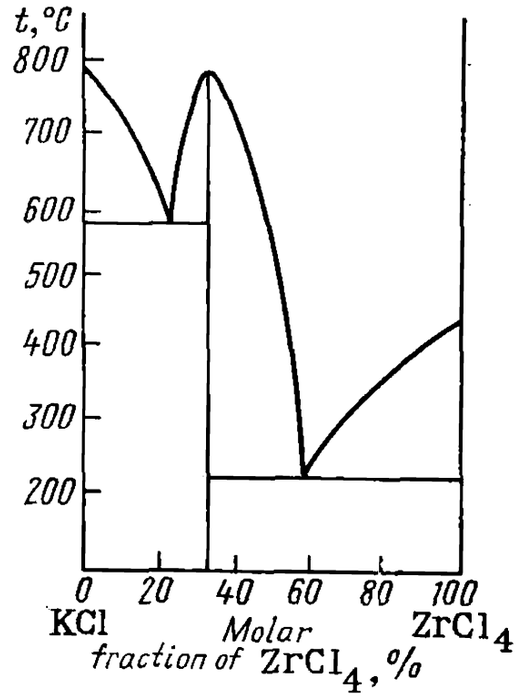


Fig. 68. Phase diagram of the system KCl-$ZrCl_4$

15. Give equations of half-reactions and the standard electrode potentials of the systems Ti^{3+}/Ti, ZrO^{2+}/Zr, HfO^{2+}/Hf.

(a) Titanium, zirconium and hafnium do not react with water, dilute sulphuric and hydrochloric acids in normal conditions. But in the presence of the F^- ions, they react even with weak acids, such as acetic acid. Explain this fact.

(b) These metals are most readily soluble in hydrofluoric acid and in a mixture of hydrofluoric and nitric acids. Explain.

Experiment 9. Depassivating titanium in the presence of fluoric ions. (Use the hood!) Act with dilute acetic acid on titanium powder. Pay attention to the absence of reaction. Add a small amount of NH_4F into the test tube. Explain your observations.

16. Calculate the change in the Gibbs free energy at 1000 K in reduction of ZrO_2(c) and $ZrCl_4$(g) to metallic zirconium by magnesium, using the following data:

	Mg (l)	ZrO_2 (c)	MgO (c)	$ZrCl_4$ (g)	$MgCl_2$ (l)
ΔG°_{1000}, kJ/mole . . .	−6.3	−903.7	−493.9	−740.6	−481.8

(a) Which of said reactions is the most probable thermodynamically and which of them is the main method of obtaining zirconium in industry?

(b) What reactions underlie the methods for obtaining titanium? The thermal (carbon) method is not used to obtain Ti, Zr and Hf. Why?

17. The formation of coloured octahedral complexes of the ion $Ti(O_2)^{2+}$ (peroxytitanyl ion) is characteristic of titanium(IV). In the presence of sulphuric acid the peroxytitanyl ion forms the complex $[TiO_2(SO_4)_2]^{2-}$ and in the presence of hydrochloric acid, the complex $[TiO_2Cl_4]^{2-}$.

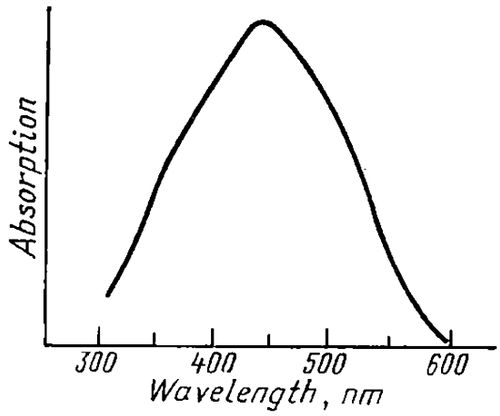


Fig. 69. Absorption spectrum of the $Ti(O_2)^{2+}$ ion complexes

The complexes of the peroxytitanyl ion absorb maximum at 435 nm (Fig. 69).

(a) Determine the colour of the complexes of $Ti(O_2)^{2+}$.

(b) The formation of these peroxy complexes can be used for analytical detection of Ti(IV) compounds as well as of hydrogen peroxide in solution. The fluoride ion interferes with the determination. The vanishing colour of solution on the addition of NH_4F is another indication that a derivative of Ti(IV) is present. What reaction destroys the colour?

Experiment 10. Formation of complexes of the ion $[Ti(O_2)]^{2+}$. Test for Ti(IV) compounds. Add 2-3 drops of a 3 per cent solution of H_2O_2 to a few drops of titanyl sulphate solution acidified with sulphuric acid. Explain the development of orange-yellow colour and its disappearance on the addition of NH_4F.

9.3. Compounds of Ti(III)

18. (a) Explain the structure of TiF_3, Ti_2O_3, $TiBr_3$, TiI_3, $TiCl_3$ from the standpoint of the characteristic coordination number of Ti(III).

(b) $TiCl_3$ is a crystalline substance and $TiCl_4$ is a liquid in normal conditions. Explain this fact.

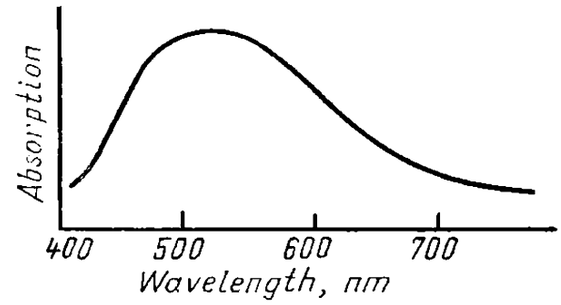


Fig. 70. Absorption spectrum of the ion $Ti(OH_2)_6^{3+}$ in the visible region

19. Figure 70 shows a curve illustrating the absorption of the $Ti(OH_2)_6^{3+}$ complex in the visible region of the spectrum.

(a) Draw the energy diagram of the molecular orbitals of this complex.

(b) What electron transition accounts for the absorption maximum (Fig. 70)?

(c) What is the colour of the $Ti(OH_2)_6^{3+}$ ion?

20. The wavelength of the maximum absorption in the spectrum of the titanium-cesium alums $Cs_2SO_4 \cdot Ti_2(SO_4)_3 \cdot 24H_2O$ is at 500 nm.

(a) What is the colour of the alum crystals?

(b) The presence of what unit cells (complexes) accounts for the colour of crystals?

21. Depending on the nature of the ligand, compounds of Ti(III) are coloured in different shades of red-violet:

$Ti(OH_2)_6^{3+}$	$Ti(OH)_3$	TiF_3
purple	cherry-red	purple-red
TiF_6^{3-}	$TiCl_3$	$TiBr_3$
violet	violet	red-violet

Explain the similarity of colouration of the substances. Take into consideration that the energy of splitting of the octahedral complexes (unit cells) of titanium(III) with the ligands Br^-, Cl^-, F^-, OH^-, and OH_2 is 180-240 kJ/mole.

22. Give examples of reactions for obtaining Ti(III) compounds.

Experiment 11. Obtaining $Ti(OH_2)_6^{3+}$ derivatives. (a) Place 2-3 granules of zinc into an acidified solution of a titanium(IV) compound: the solution colour changes. Explain. Transfer quickly the solution obtained into another test tube, stopper it and keep for the next experiment.

(b) Add sulphuric or hydrochloric acid to titanium powder. Observe the absence of a reaction. Explain the development of colour in the solution on heating.

23. Three hydrate isomers of $TiCl_3 \cdot 6H_2O$ are known. One of them is violet, the other two are green with different hues. Act with $AgNO_3$ solution on all the three isomers: 3, 2 and 1 mole of AgCl precipitate respectively (per mole of the corresponding isomer). What is the composition of the inner and outer spheres of the isomers?

24. Give equations of half-reactions and the standard oxidation-reduction potentials of the systems TiO^{2+}/Ti^{3+} and MnO_4^-/Mn^{2+} in an acid medium. Will the colour change if acidified solutions of $TiCl_3$ and $KMnO_4$ are mixed together?

Experiment 12. Reducing properties of titanium(III) compounds. (a) Add, by drops, $KMnO_4$ solution to the solution of Ti(III) compound obtained earlier. Explain your observations.

(b) Obtain Ti(III) hydroxide by an exchange reaction. Stir carefully the precipitate with a glass rod. Explain your observations.

25. Calculate ΔH°_{298} and ΔS°_{298} of the reactions:

$$2TiCl_3(c) = TiCl_2(c) + TiCl_4(g); \quad 2TiCl_2(c) = TiCl_4(g) + Ti(c)$$

(a) What factor, enthalpy or entropy, determines the course of the reactions? Explain your answer.

(b) Calculate the temperature of the processes at $p_{TiCl_4} = 101.325$ kPa. What chloride disproportionates at higher temperature?

26. How does the chemical nature of similar compounds change with the increasing oxidation state of titanium in the series: TiO-Ti_2O_3-TiO_2; $Ti(OH)_2$-$Ti(OH)_3$-$Ti(OH)_4$; $TiCl_2$-$TiCl_3$-$TiCl_4$.

Illustrate your answer by equations of the corresponding reactions.

Experiment 13. The study of acid-base properties of titanium(III) hydroxide. Obtain titanium(III) hydroxide and prove the possibility of its reaction with acids and alkalis.

27. The action of hydrogen fluoride on titanium with heating gives titanium fluoride. According to X-ray structural analysis its crystals are the ReO_3 type. The study of the magnetic properties indicates that the compound is paramagnetic (one unpaired electron per one atom of Ti). What fluoride of titanium is formed? Write the reaction equation.

CHAPTER 10

d-Elements of Group V

10.1 Elements and Simple Substances

1. Construct graphs showing the variation of radii of atoms and E^{5+} ions and ionization energy with atomic number of the elements in the vanadium subgroup. Explain the curves.

(a) What accounts for the similarity of the atomic and ionic radii of niobium and tantalum and how does this similarity affect the properties of elements in the series V-Nb-Ta?

(b) What oxidation states are most characteristic of vanadium, niobium and tantalum? How does the stability of the highest oxidation state change in the series V-Nb-Ta?

(c) Why are Nb and Ta found together with the same minerals? Name the main minerals of vanadium, niobium and tantalum.

2. How do the values of enthalpy of melting and sublimation, melting and boiling points, and density of metals change in the series V-Nb-Ta? Explain your answer.

3. (a) Determine the thermodynamic probability of obtaining vanadium, niobium and tantalum from E_2O_5 oxides by metallothermy (see Fig. 67). What metallothermic reactions are used to obtain these metals from their oxides?

(b) Why cannot the carbon metallothermic method be used to obtain pure vanadium?

(c) Which of the following halides is more suitable to obtain vanadium by thermic decomposition of compound, if

	VF_2 (c)	VCl_2 (c)	VBr_2 (c)	VI_2 (c)
ΔG°_{298}, kJ/mole . .	−791	−406	−389	−264

10.2 Compounds of V(II)

4. What is the most characteristic coordination number of ions of 3*d*-elements with d^3-electron configuration?

(a) Draw energy level diagrams and distribute valent electrons in σ-molecular orbitals of the octahedral complexes (unit cells) $V(NH_3)_6^{2+}$, $V(OH_2)_6^{2+}$, VF_6^{4-}.

(b) Describe the structure and the states of aggregation of VO, VF_2, VCl_2, $V(OH)_2$ in normal conditions.

5. Figure 71 shows the absorption spectrum of the $V(OH_2)_6^{2+}$ complex.

(a) What colour is the aquo complex?

(b) How are water molecules coordinated in the crystals of $VSO_4 \cdot 7H_2O$, $M^I_2SO_4 \cdot VSO_4 \cdot 6H_2O$ ($M^I = K^+$, Na^+, NH_4^+)? What is the colour of these crystal hydrates?

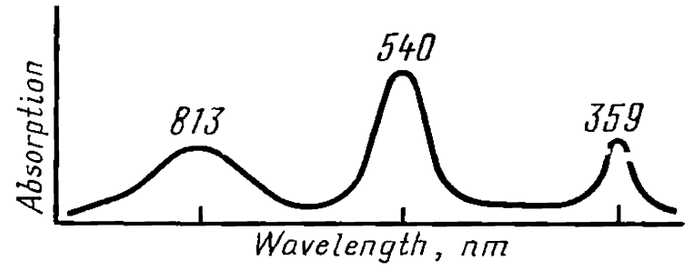


Fig. 71. Absorption spectrum of $V(OH_2)_6^{2+}$

Experiment 1. Obtaining compounds of V(II), V(III) and V(IV). Add concentrated hydrochloric acid and a few granules of zinc to a saturated ammonium vanadate(V) solution (or its suspension in water). Observe the sequence of changing colour, from complete absence of colour to blue, green, and violet. Take samples of solution of each colour into test tubes and keep for future experiments. Write equations for the reactions, assuming that the VO_3^- ion is reduced first to the complex $[VO(OH_2)_5]^{2+}$, then to $[V(OH_2)_6]^{3+}$ and $[V(OH_2)_6]^{2+}$. Which complex is violet?

6. What are the acid-base properties of the oxide and hydroxide of vanadium(II)? Check your answer by carrying out the following experiment.

Experiment 2. Obtaining vanadium(II) hydroxide and studying its acid-base properties. Use the violet solution produced in Experiment 1 to obtain vanadium(II) hydroxide by an exchange reaction. Determine its acid-base properties. Take into consideration that partial dissolution of the precipitate in excess alkali is due to the amphoteric properties of zinc hydroxide. (The Zn^{2+} ion is formed by oxidation of zinc metal in Experiment 1).

7. Give equations of half-reactions and standard oxidation-reduction potentials of the systems V^{3+}/V^{2+}, MnO_4^-/Mn^{2+}, $O_2/2H_2O$ in an acid medium.

(a) Will the +2 oxidation state of vanadium change in solution under the action of air oxygen or $KMnO_4$ solution?

(b) Why do acid solutions of compounds V(II) change their colour with time (in the absence of air)?

Experiment 3. Reducing properties of vanadium(II). Add, by drops, potassium manganate(VII) solution to a solution of a vanadium(II) compound. Explain your observations.

10.3 Compounds of V(III)

8. What is the most characteristic coordination number for vanadium in the +3 oxidation state?

(a) Distribute electrons in the orbitals of octahedral complexes (unit cells) $V(OH_2)_6^{3+}$, VCl_6^{3-}, $V(NH_3)_6^{3+}$, VF_6^{3-}.

9. Describe the structure of V_2O_3, VF_3, VCl_3.

10. Figure 72 shows the absorption spectrum of the complex $[V(OH_2)_6]^{3+}$. What is the colour of the $V(OH_2)_6^{3+}$ ion?

(a) Consider Figs. 71 and 72. Why does the absorption maximum of the $V(OH_2)_6^{3+}$ ion shift to the region of shorter wavelengths compared with the ion $V(OH_2)_6^{2+}$?

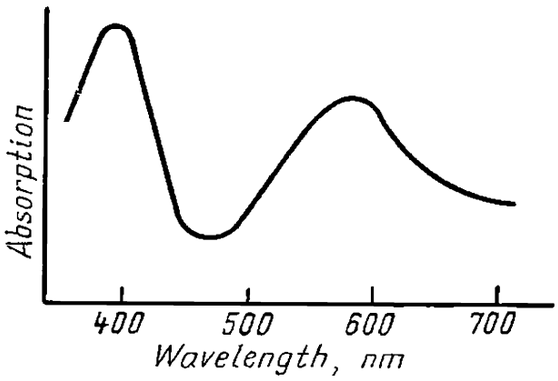


Fig. 72. Absorption spectrum of the ion $V(OH_2)_6^{3+}$

(b) Which of the solutions obtained in Experiment 1 contains the $V(OH_2)_6^{3+}$ ion?

(c) How are water molecules coordinated in the crystals of $VCl_3 \cdot 6H_2O$, $RbV(SO_4)_2 \cdot 12H_2O$, $KV(SO_4)_2 \cdot 12H_2O$? What is the colour of these crystal hydrates?

Experiment 4. Obtaining vanadium(III) derivatives. Add potassium iodide solution to a saturated ammonium vanadate(V) solution acidified with sulphuric acid. Explain the changes observed. Isolate the liberated iodine by benzene (or bind with thiosulphate) and determine the colour of the aquo complex of vanadium(III).

11. Figure 73 shows the phase diagram of the system CsCl-VCl_3.

(a) What acid-base properties does VCl_3 show in the reaction with CsCl and what compounds are formed in this reaction?

(b) Describe the structure of the complexes formed in the system.

(c) Explain the changing stability of compounds in the series Na_3VCl_6-K_3VCl_6-Rb_3VCl_6-Cs_3VCl_6. The enthalpies of formation of the compounds from binary chlorides are

	Na_3VCl_6	K_3VCl_6	Rb_3VCl_6	Cs_3VCl_6
ΔH°_{298}, kJ/mole	−25.5	−60.2	−82.8	−86.6

10.4. Compounds of V(IV)

12. Explain the structure of VO_2 and VCl_4 and determine their state of aggregation in normal conditions.

13. The length of the bonds V—O and V—OH_2 in the $[VO(OH_2)_5]^{2+}$ ion is 0.167 and 0.23 nm respectively.

(a) Describe the structure of the ion.

(b) Using the results of Experiment 1, determine the colour of the $[VO(OH_2)_5]^{2+}$ ion.

14. Write equations of reactions for obtaining vanadium(IV) derivatives from compounds of vanadium(V) and vanadium(III).

Experiment 5. Obtaining V(IV) derivatives from V(V) compounds. Place vanadium(V) oxide into a dry test tube and add 1-2 ml of concentrated hydrochloric acid. Prove experimentally that the evolving gas is chlorine. Write the equation of the reaction assuming that vanadyl(IV) chloride is formed.

15. Both cation and anion complexes are known for vanadium(IV).

(a) What are the acid-base properties of VO_2? Complete the following equations:

$$VO_2 + H_2SO_4 \rightarrow; \quad VO_2 + KOH \rightarrow$$

assuming the formation of $[VO(OH_2)_5]^{2+}$ and $V_4O_9^{2-}$.

(b) Write the equation of hydrolysis of VCl_4 and $VOCl_2$.

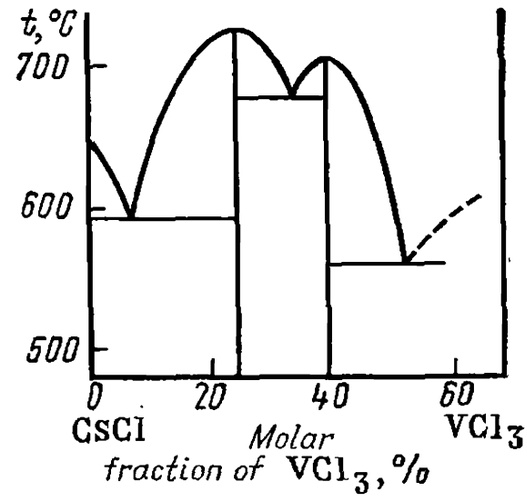


Fig. 73. Phase diagram of the system CsCl-VCl_3

Experiment 6. Obtaining $VO(OH)_2$ and its properties. Add, by drops, a dilute alkali solution to $[VO(OH_2)_5]Cl_2$ solution obtained in Experiment 1 to precipitate $VO(OH)_2$. Try the action of excess alkali and acid on the precipitate. Explain your observations.

Experiment 7. Hydrolysis of VCl_4. Open a bottle containing VCl_4. Explain your observations.

10.5. Compounds of V(V), Nb(V) and Ta(V)

16. Give examples of oxides, oxyhalides and halides and of the corresponding complexes of V(V), Nb(V) and Ta(V). What are the acid-base properties of binary and ternary compounds of E(V)? Exemplify your answer by reaction equations.

17. Below follow the physical properties of pentahalides:

	VF_5 (c)	NbF_5 (c)	$NbCl_5$ (c)	TaF_5 (c)	$TaCl_5$ (c)
M. p., °C	19.5	80	205	95.1	217
B. p., °C	48.3	233	254	230	240
S°_{298}, J/deg mole . .	192	157	226	170	238
$\Delta H^\bullet_{f_{298}}$, kJ/mole. . .	−1481	−1814	−798	−1904	−858

(a) Describe the structure of the pentahalides and their states of aggregation in normal conditions.

(b) Explain similarity of the pentahalides of niobium and tantalum.

18. Molten fluorides EF_5 (E = V, Nb, Ta) fall to ions:

$$EF_5 + EF_5 \rightleftarrows EF_4^+ + EF_6^-$$

and they can therefore be used as non-aqueous solvents.

(a) What compounds are formed by dissolution of KF and PF_5 in EF_5? What are the acid-base properties of EF_5 in this process?

19. The vanadium and tantalum complexes can be arranged in the following series in the order of their decreasing stability: $VF_6^{3-} \gg VCl_6^{3-} > VBr_6^{3-} > VI_6^{3-}$; $NbF_6^- \gg NbCl_6^- > NbBr_6^- > NbI_6^-$; $TaF_6^- \gg TaCl_6^- > TaBr_6^- > TaI_6^-$.

The oxides Nb_2O_5 and Ta_2O_5 do not react with hydrochloric acid but readily dissolve in hydrofluoric acid. Why?

20. Write equations for the corresponding half-reactions and standard potentials E° in an acid medium of the following systems VO_2^+/V, Nb_2O_5/Nb and Ta_2O_5/Ta.

(a) Why do these metals not react with water or dilute sulphuric acid in normal conditions despite their negative electrode potentials?

(b) Metals most readily dissolve in hydrofluoric acid or in a mixture of hydrofluoric and concentrated nitric acid. Explain.

(c) The $[NbOF_5]^{2-}$ complex ion is formed in the reaction of niobium with a 30 per cent HF solution. The $[NbF_6]^-$ complex ion is formed at higher concentrations of HF and $[NbF_7]^{2-}$ ion may be formed by dissolution of niobium in anhydrous HF. Write equations of the corresponding reactions.

(d) What conditions are required to convert vanadium, niobium and tantalum into EO_4^{3-} complex ions?

21. Calculate ΔG°_{298} of decomposition of NH_4VO_3(c) with formation of vanadium(V) oxide and gaseous H_3N and H_2O if $\Delta H^\circ_{298} = 215.8$ kJ/mole V_2O_5, $\Delta S^\circ_{298} = 423.7$ J/deg·mole V_2O_5.

(a) What factor, enthalpy or entropy, determines the direction of the process? Explain your answer. Under what conditions does the process occur?

(b) At what temperature of decomposition of NH_4VO_3 does the partial pressure rise to 101.325 kPa?

Experiment 8. Obtaining vanadium(V) oxide by thermal decomposition of NH_4VO_3. (Use the hood!) Calcine a small quantity of NH_4VO_3 in a porcelain dish with stirring continually with a glass rod. (Heat on a sand bath until the mass turns orange-red. Do not overheat the precipitate to black.) Identify the evolving gas. Cool the obtained product, place it into a test tube and keep for next experiments. Write the reaction equation.

Experiment 9. Chemical nature of vanadium(V) oxide. (a) Add several drops of violet litmus to distilled water in two test tubes. Put a few grains of V_2O_5 into one of them. Explain your observations.

(b) Put a few grains of V_2O_5 into two test tubes. Add 1-2 ml of dilute alkali solution into one of them and concentrated sulphuric acid into the other, and heat. Explain your observations.

22. Figure 74 shows the phase diagram of the CaO-Nb_2O_5 system.
(a) What compounds can be found in this system?
(b) Explain the structure of $NaNbO_3$, $NaTaO_3$ (perovskite structure type) and $Mn(TaO_3)_2$, $Fe(NbO_3)_2$ (rutile structure type); which of them are mixed oxides?

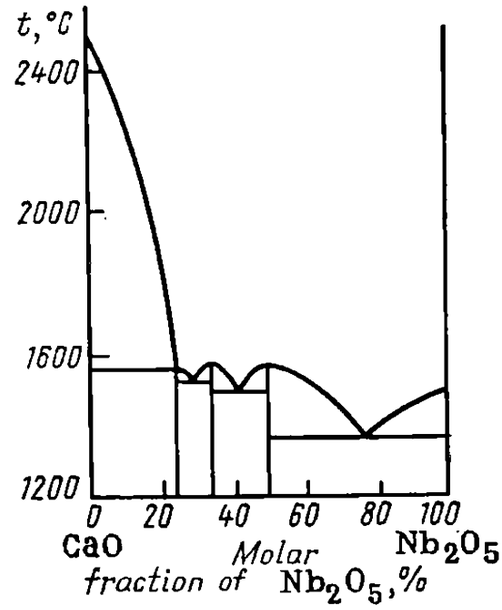


Fig. 74. Phase diagram of the system CaO-Nb_2O_5

23. The formation of coloured peroxyvanadate(V) complex ions $[VO_2(O_2)_2]^{3-}$, $[V(O_2)_4]^{3-}$, $[VO(O_2)_3]^{3-}$ in the reaction of VO_3^- with hydrogen peroxide is characteristic of vanadium(V). Describe the structure of these ions.

Experiment 12. Obtaining vanadium(V) peroxy complexes. (Test for oxyvanadate(V) ion). Add water and concentrated alkali solution respectively into two test tubes containing V_2O_5. Add a 3 per cent hydrogen peroxide solution by drops. Explain the colour change. Assume that yellow $[VO_2(O_2)_2]^{3-}$ ion is formed in one test tube and blue-violet $[V(O_2)_4]^{3-}$ ion in the other.

24. How do the acid-base properties of compounds change with the increasing oxidation state of vanadium in the series: VO-V_2O_3-VO_2-V_2O_5; $V(OH)_2$-$V(OH)_3$-$VO(OH)_2$-HVO_3; VF_2-VF_3-VF_4-VF_5? Prove your answer by examples of reaction equations.

10.6. Cluster Compounds of Nb and Ta

25. Describe the structure of the following halides: $EHal_{1.88}$ (E_6Hal_{11}), $EHal_{2.33}$ (E_6Hal_{14}), $EHal_{2.5}$ (E_6Hal_{15}), $EHal_{2.67}$ (E_3Hal_8), where E = Nb, Ta.
(a) Why does the solution of $AgNO_3$ precipitate only two moles of the chloride ion per mole of the chloride from solutions of Nb_6Cl_{14} and Ta_6Cl_{14}?
(b) Why are cluster compounds most characteristic of Nb and Ta and are not characteristic of V?

CHAPTER 11

d-Elements of Group VI

11.1. Elements and Simple Substances

1. Construct a graph showing the variation of the atomic and ionic radii and ionization energy with the atomic number of elements of the chromium subgroup.

(a) Explain the curves.

(b) What are the oxidation states of Cr, Mo and W? How does the ability of the elements to pass to the highest oxidation state change in the series Cr-Mo-W?

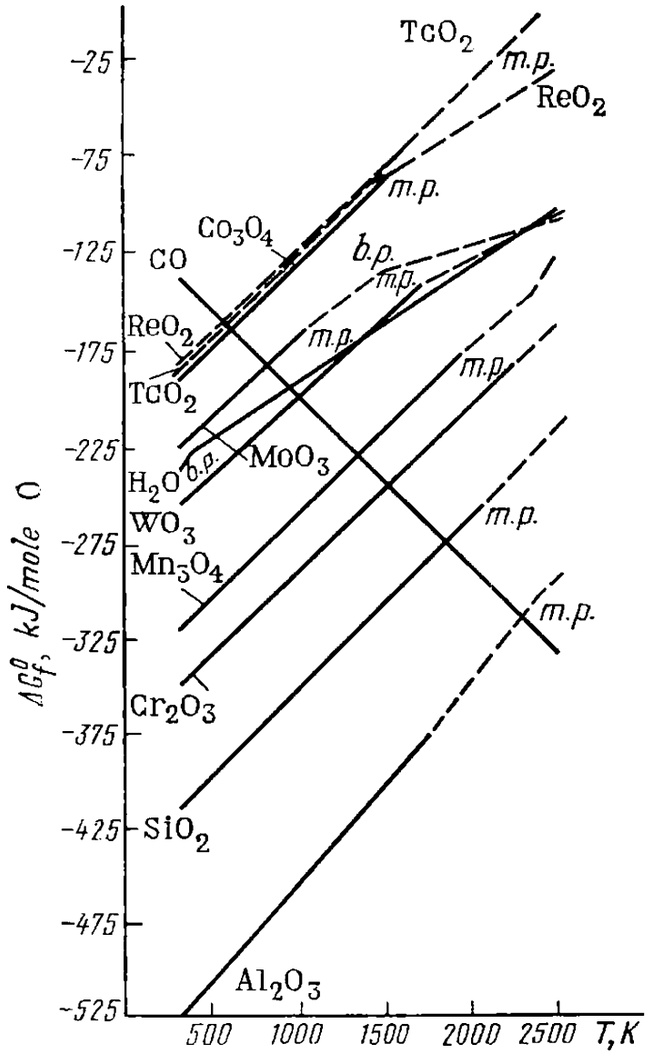


Fig. 75. Variation of ΔG_f° of some oxides with temperature

2. Explain the character of variation in the enthalpy of melting and sublimation, boiling and melting points of the metals in the series Cr-Mo-W.

3. Figure 75 shows the variation of the Gibbs free energy of formation of some oxides with temperature.

(a) What simple substances (of those given in the diagram) can be used to reduce chromium from Cr_2O_3 and tungsten from WO_3?

(b) How are chromium, molybdenum and tungsten obtained in industry and laboratory?

(c) What are ferrochromium, ferromolybdenum and ferrotungsten and how are they obtained in industry?

4. Write equations of half-reactions and standard oxidation-reduction potentials E°_{298} in the acid medium of the systems Cr^{3+}/Cr, MoO_4^{2-}/Mo and WO_4^{2-}/W.

(a) How does the chemical activity of the metals change in the series Cr-Mo-W? Explain your answer. Illustrate your answer by reaction equations.

(b) Molybdenum and tungsten react most easily with a mixture of $HF + HNO_3$. Explain why.

(c) In what conditions can the metals of 4*d*- and 5*d*-elements be dissolved by acids and alkalies?

Experiment 1. The attitude of metals to acids. (a) Act on chromium (tungsten wire) with dilute hydrochloric and sulphuric acids. Explain your observations.

(b) Put a piece of chromium into concentrated nitric acid for 1-2 minutes. Discard the solution and wash the metal with water. Try the attitude of chromium to dilute hydrochloric acid. Explain the absence of visible chemical reaction.

5. What coordination number is characteristic of Cr(II)?

6. Give electron configurations of the complexes $Cr(OH_2)_6^{2+}$ and $Cr(NH_3)_6^{2+}$.

(a) Determine what kind of complexes they are: high- or low-spin, para- or diamagnetic.

(b) Why are the high-spin octahedral complexes (unit cells) of chromium(II) characterized by tetragonal distortion (two bonds differ from the remaining four in their length)? Describe the structure of $CrCl_2$ (d_{CrCl} = 0.239 nm and 0.290 nm).

7. The absorption maximum at 709 nm in the spectrum of $Cr(OH_2)_6^{2+}$ complex corresponds to the electron transfer. What is the colour of the aquo complex?

Experiment 2. Formation of chromium(II) aquo complexes. Place a few zinc granules into a flask, add 2-3 ml of dilute chromium(III) chloride solution acidified with hydrochloric acid and a thin layer of acetone. The colour of the solution changes. Explain. Pour the solution quickly into a test tube, stopper it and keep for future experiments.

8. The colour of solutions of chromium(II) compounds change on exposure to air.

(a) Explain this fact. To prove your answer give oxidation-reduction potentials of the corresponding systems.

(b) Solution of $CrCl_2$ acidified with hydrochloric acid is used for the absorption of oxygen. Why?

(c) The colour of chromium(II) compounds changes even if the solution is not exposed to air. Explain.

(d) Explain the high reducing activity of $Cr(OH_2)_6^{2+}$.

Experiment 3. Reducing properties of chromium(II) compounds. (a) Place the solution of chromium(II) compound obtained in the previous experiment in a test tube. Explain the changing colour of the solution when shaken.

(b) Add chromium(II) chloride into a test tube containing alkali solution. Shake. Explain your observations.

9. In the chemical analysis of dihalides of molybdenum and tungsten ($MoCl_2$, $MoBr_2$, MoI_2 and WCl_2, WBr_2, WI_2), in contrast to $CrCl_2$, the ion Ag^+ fails to reveal all halide ions corresponding to the dihalide composition.

(a) Describe the structure of dihalides of Mo and W and explain the stated experimental fact.

(b) What type of compounds are the dihalides of Mo and W?

Explain the differences between the structure of chromium dihalides and of dihalides of molybdenum and tungsten.

11.3. Compounds of Cr(III), Mo(III) and W(III)

10. Calculate the stabilization energy of the ligand crystal field (in Δ units) of high-spin ion of Cr(III) in tetrahedral and octahedral environment.

What coordination (tetrahedral or octahedral) is more advantageous for Cr(III) in its compounds?

11. (a) Describe the electron configuration of the Cr^{3+} ion. What coordination number is characteristic of Cr(III)?

(b) Explain the structure of chromium(III) complexes (unit cells) from the standpoint of valency bond theory.

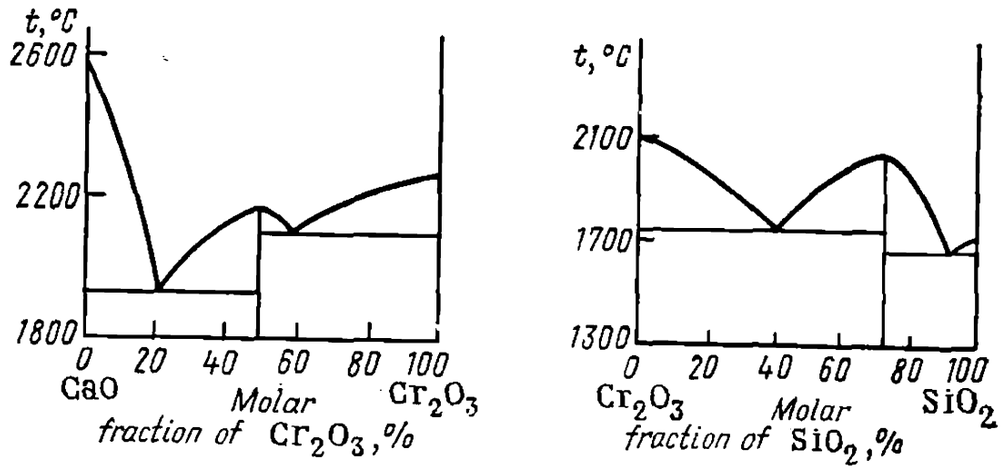


Fig. 76. Phase diagrams of the systems $CaO-Cr_2O_3$ and $Cr_2O_3-SiO_2$

(c) What molecular orbitals do the electrons of Cr(III) octahedral complexes occupy? Give the electron configurations of aquo, chlorine, cyan, fluorine, hydroxy, ammino, bromine and thiocyanate complexes of chromium(III).

(d) What complexes are they, para- or diamagnetic?

(e) Write equations of the reactions by which the complexes are obtained.

12. The results of the studies of $CaO-Cr_2O_3$ and $Cr_2O_3-SiO_2$ systems are shown in Fig. 76.

(a) What compounds are formed in these systems? Write equations of reactions by which they are obtained and characterize the acid-base properties of chromium(III) oxide.

(b) Calculate ΔG°_{298} of formation of $Ca(CrO_2)_2$ and $Cr_2(SO_4)_3$ from the oxides. Using the data obtained, characterize the acid-base properties of Cr_2O_3.

13. (a) In what form does the Cr^{3+} ion exist in acid and alkali solutions? Give equations of reactions illustrating the acid-base properties of chromium(III) hydroxide.

(b) Calcined Cr_2O_3 is less chemically active than freshly obtained $Cr(OH)_3$. Explain why.

14. Write the equation of the reaction for obtaining Cr_2O_3 by thermal decomposition of $(NH_4)_2Cr_2O_7$. How does the process depend on the enthalpy and entropy factors? Is this process reversible?

Experiment 4. Obtaining chromium(III) oxide (chromic oxide) and its properties. (Use the hood!) (a) Fix a test tube containing ground crystals of $(NH_4)_2Cr_2O_7$ in a stand in the inclined position (with the test tube mouth away from your mates and yourselves). Heat the upper layer until the reaction begins and stop heating. Explain your observations (spontaneous heating, evolution of gas, the change in colour). Try the action of acid and alkali on the Cr_2O_3 obtained.

(b) Melt $K_2S_2O_7$ in a crucible and add a small amount of Cr_2O_3. Continue heating to dissolve all the oxide. Cool the melt and transfer a small portion of it into water. Explain your observations.

Experiment 5. Acid-base properties of chromium(III) hydroxide. Obtain chromium(III) hydroxide and prove experimentally its amphoteric properties.

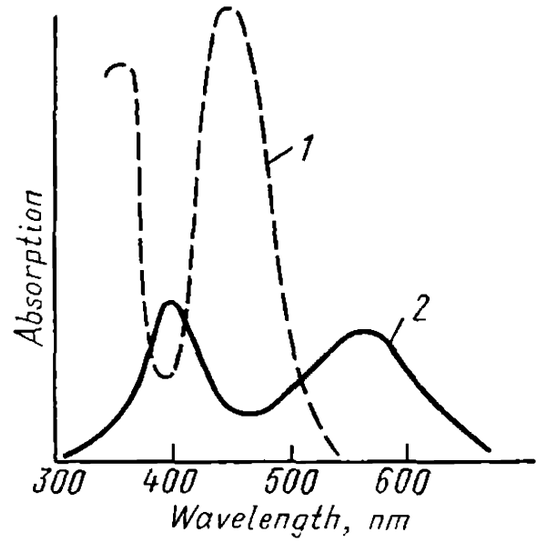


Fig. 77. Absorption spectra of the ion $Cr(NH_3)_6^{3+}$ (*1*) and $Cr(OH_2)_6^{3+}$ (*2*)

15. Write the formulas of the simplest oxychromates(III) of sodium, calcium, iron(II), magnesium, cobalt(II).

(a) Which of them are salts and which mixed oxides?

(b) Write the equation of the reaction for the obtaining and hydrolysis of sodium chromate(III).

16. The rate of exchange of the ligand molecules of H_2O in the ion $Cr(OH_2)_6^{3+}$ for water molecules from solution

$$Cr(OH_2)_6^{3+} + H_2\overset{*}{O} \rightleftarrows [Cr(OH_2)_5(\overset{*}{O}H_2)]^{3+} + H_2O$$

is about 2500 times slower than the rate of similar exchange in the ion $Cr(OH_2)_6^{2+}$.

(a) Which of these complexes is inert and which is labile?

(b) Explain the different reactivity of Cr(III) and Cr(II) complexes.

17. Figure 77 shows the absorption spectra of the complex ions $Cr(NH_3)_6^{3+}$ and $Cr(OH_2)_6^{3+}$.

(a) Predict their colour if they absorb maximum at 463 and 351 nm (hexaammino complex) and at 574 and 407 nm (hexaaquo complex) of chromium(III).

(b) Explain the displacement of the absorption maximum in the aquo complex spectrum to longer wavelengths compared with the ammino complex.

(c) When the NH_3 molecules are replaced gradually by H_2O molecules, the colour of the chromium(III) complexes changes from yellow to violet. Explain why.

(d) X-ray structural analysis of alums shows that this structure might be $[E^{I}(OH_2)_6][E^{III}(OH_2)_6][SO_4]_2$, where E^{I} is the alkali metal (E^{III} is Cr, Al, Fe, V or Ti). Predict the colour of chrome alum.

Experiment 6. Obtaining chromic potassium sulphate. (Use the hood!) Chromic potassium sulphate can be obtained by reducing potassium dichromate(VI) with ethyl alcohol in the presence of sulphuric acid. Write the reaction equation assuming that the alcohol is reduced to aldehyde.

Place 25 ml of a 10 per cent solution of $K_2Cr_2O_7$ into a 50-ml beaker and add 10 ml of concentrated H_2SO_4 (density, 1.84 g/cc) by small portions while continually stirring and cooling the solution in snow or cold running water.

Next add, also dropwise and stirring, ethyl alcohol until the solution turns dark violet. Ensure that the temperature does not rise to 40°C. The reaction is complete when the acetaldehyde smell disappears.

Keep the solution for the next experiment. Separate the precipitated crystals on a funnel with suction and dry in filter paper. Note the colour and the shapes of the crystals. Prove that the K^+, $Cr(OH_2)_6^{3+}$ and SO_4^{2-} ions are contained in the crystals. (Use the flame test to detect K^+.)

Experiment 7. Obtaining aquo ammino complexes of chromium(III). Add a saturated solution of NH_4Cl and an ammonia solution to a solution of $CrCl_3$. Explain the colour change.

18. Three isomers are known to have the composition of $CrCl_3 \times \times 6H_2O$. One of them is violet while the other two are different shades of green. As the solutions of the violet, light green and dark green isomers are acted upon with $AgNO_3$ solution, they precipitate 3, 2 and 1 mole of AgCl per mole of the corresponding crystal hydrates respectively.

(a) What type of isomerism does this experiment demonstrate? What is the composition of the inner and the outer spheres of the isomers?

(b) Why are the isomers of different colour?

Experiment 8. Obtaining hydrate isomers of chromium(III). Effect of the ligand nature on the complex colour. Heat a violet solution of chromium(III) hexaaquochloride until its colour changes. As the solution cools its colour is gradually restored.

19. Figure 78 shows the temperature effect on the degree of hydrolysis of $CrCl_3$. Write the equation of hydrolysis and explain the curve.

Experiment 9. Hydrolysis of chromium(III) compounds. (a) Prepare solutions of $CrCl_3$ and $Cr(NO_3)_3$. Measure the pH of the solutions at normal temperature and with heating. Explain your observations.

(b) Try if possible to obtain Cr_2S_3 and $Cr_2(CO_3)_3$ by exchange reactions in solution. Test the action of acid and alkali on the precipitates obtained. Explain your observations.

20. (a) What compounds are formed in the KCl-$CrCl_3$ system? Write reaction equations.

(b) What is the role of the acid-base properties of KCl and $CrCl_3$ in these processes?

(c) Describe the structure of the complexes found in the KCl-$CrCl_3$ system.

21. According to calculations and experimental data, the enthalpy of formation of hexachlorochromates(III) of sodium, potassium, rubidium and cesium from binary chlorides is 2.9, —46.0, —69.9 and —76.99 kJ/mole respectively.

How does the stability of similar compounds depend on the nature of the alkali metal? Explain.

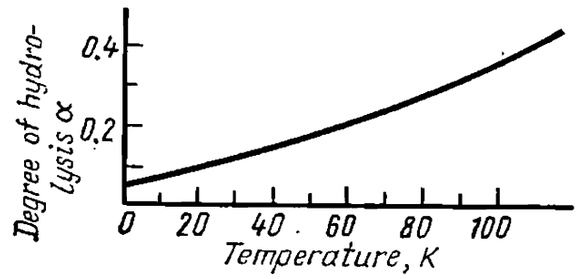


Fig. 78. Variation of degree of hydrolysis of $Cr(OH_2)_6Cl_3$ with temperature

22. Explain the following experimental data. The distance between Cr atoms (0.310 nm) in the $Cr_2Cl_9^{3-}$ ion is 0.07 nm greater than that between W atoms (0.240 nm) in the $W_2Cl_9^{3-}$ ion. The W—W distance in the $W_2Cl_9^{3-}$ ion is smaller than that in tungsten metal (0.274-0.282 nm). According to magnetochemical studies, the $Cr_2Cl_9^{3-}$ ion is paramagnetic (three unpaired electrons per Cr atom) while the $W_2Cl_9^{3-}$ ion is diamagnetic.

11.4. Compounds of Cr(VI), Mo(VI) and W(VI)

23. Give examples of compounds and the corresponding complexes of Cr(VI), Mo(VI) and W(VI).

(a) What ligands stabilize the highest oxidation states of the elements?

(b) How does ΔG_f° of similar compounds of chromium(VI) and its analogues [for example, EO_3(c) and EO_4^{2-} (sln)] vary in the subgroup?

(c) What is the acid-base nature of binary and ternary compounds of E(VI)? Illustrate your answer by reaction equations.

24. Describe the structure of CrO_4^{2-}, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ and CrO_3.

(a) What conditions promote polymerization of the CrO_4^{2-} ion in solution?

(b) What is the colour of the CrO_4^{2-} ion if it absorbs in the region of 400-420 nm (Fig. 79)?

(c) How does the colour of the CrO_4^{2-} ion change in its dimerization (Fig. 79) and polymerization?

Experiment 10. Obtaining chromium trioxide. (Use the hood!) Place a saturated solution of sodium (potassium) dichromate into a test tube, cool it in snow or running cold water, and gradually add, carefully with stirring, concentrated sulphuric acid. Dark-red needle crystals precipitate. Separate them on a Schott funnel and

transfer by a spatula into a bottle fitted with a ground-in stopper.

Experiment 11. Acid-base properties of CrO_3 and CrO_2Cl_2. (a) Place CrO_3 into two separate test tubes and act with water and alkali respectively.

(b) Add 2-3 drops of CrO_2Cl_2 into the test tube containing alkali. Compare the colour of alkali solutions of CrO_3 and CrO_2Cl_2. Explain your observations.

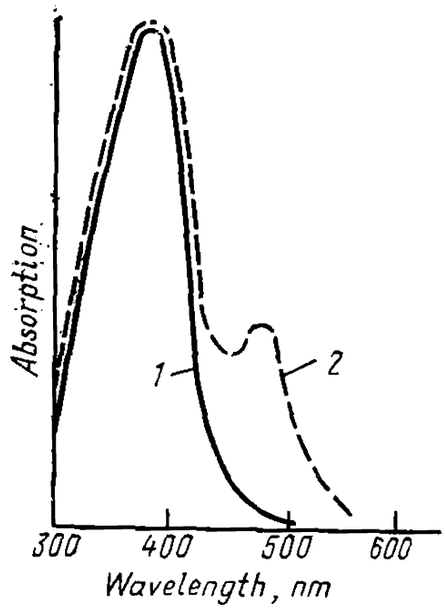


Fig. 79. Absorption spectrum of potassium chromate(VI) (*1*) and potassium dichromate(VI) (*2*)

Experiment 12. Shift of chemical equilibrium between chromate(VI) and dichromate(VI) ions. (a) Add dilute acid to K_2CrO_4 solution and alkali to $K_2Cr_2O_7$ solution. Explain your observations.

(b) Add a few drops of $BaCl_2$ solution into two separate test tubes containing solutions of chromate(VI) and dichromate(VI) of potassium. Explain your observations. Remember that $BaCrO_4$ (yellow) and $BaCr_2O_7$ (brown) differ in colour and solubility.

26. (a) Give the melting points of EO_3 and explain the character of variation of their values in the series CrO_3-MoO_3-WO_3.

(b) Calculate the variation of the Gibbs free energy of thermal decomposition of CrO_3, MoO_3 and WO_3 in standard conditions. How does the thermal stability and oxidizing activity change in the series CrO_3-MoO_3-WO_3?

Experiment 13. Comparing thermal stability of CrO_3, MoO_3 and WO_3. (Use the hood!) Using a spatula, place crystals of chromium trioxide into a dry refractory test tube and heat carefully. Identify the evolving gas. Explain your observations.

Heat a crucible containing $WO_3(MoO_3)$. Compare the behaviour of $WO_3(MoO_3)$ and CrO_3 during heating. Explain.

Experiment 14. Comparing oxidizing activity of chromium trioxide and tungsten (molybdenum) trioxide. (Use the hood!) Add a few drops of ethyl alcohol to CrO_3 and $WO_3(MoO_3)$ crystals in separate dry porcelain dishes. When does the alcohol inflame? Explain your observatins.

27. (a) Using oxidation-reduction potentials of the corresponding systems, determine the possibility of reactions: between acidified solutions of compounds of chromium(VI) and of sulphur(IV); between gaseous chlorine and an alkaline solution of chromium(III) compound. Write reaction equations.

(b) The oxidizing properties of oxychromate(VI) ions in an acid medium are stronger than in an alkaline or neutral medium. Explain why. Compounds of chromium(III) are comparatively readily oxidized in an alkaline medium, while in an acid medium the oxidation can be effected only by strong oxidants.

Experiment 15. Oxidizing properties of chromium(VI) compounds. (a) Add a solution of $NaNO_2$ or Na_2SO_3 to $K_2Cr_2O_7$ solution acidified with dilute sulphuric acid and heat slightly. Explain your observations.

(b) Add $(NH_4)_2S$ solution to $K_2Cr_2O_7$ solution. Explain your observations.

Experiment 16. Oxidizing chromium(III) compounds to chromates(VI). (a) Obtain potassium hydroxychromate(III). Add bromine water to the solution and heat slightly. Explain the changing colour of the solution.

(b) Add a drop of $Cr(NO_3)_3$ solution (not chloride!) to distilled water in a test tube. Add 5 drops of dilute sulphuric acid, 10 drops of $AgNO_3$ solution and solid ammonium persulphate (using a spatula). Heat the test tube. Explain the changing colour, remembering that the silver ion acts as a catalyst.

Experiment 17. Obtaining potassium oxychromate(VI) from chromium(III) oxide. (Use the hood and goggles!) Melt a mixture of KNO_3 and K_2CO_3 (1 : 1) on the lid of a porcelain crucible. Place a few grains of Cr_2O_3 into the melt and calcine. Explain your observations.

28. Explain the increasing corrosion resistance of metals after treating their surfaces with $K_2Cr_2O_7$ solution.

Experiment 18. Passivating metals in dichromate(VI) solution. Polish two aluminium plates with abrasive paper and degrease in alcohol. Immerse one plate into a 10 per cent potassium dichromate(VI) solution for five minutes, decant the solution and wash the plate.

Try the attitude of the both plates to dilute hydrochloric acid. Explain the decreased chemical activity of the aluminium plate after its treatment in potassium dichromate(VI).

29. Explain why chromic-sulphuric acid ($K_2Cr_2O_7 + H_2SO_4$) is used to remove organic contaminants from laboratory glassware. Why is the mixture less effective in removing inorganic contaminants?

30. Describe the structure of chromium peroxy complexes $CrO(O_2)_2L$ (L is a molecule of ether or the OH^-ion). Write equations for reactions of their formation and decomposition by water.

Experiment 19. Formation of chromium(VI) oxyperoxide $CrO(O_2)_2$. Test for chromium(VI). Add a few drops of dilute H_2SO_4, 2 ml of ether to 1-2 ml of H_2O_2 solution and shake thoroughly. Add a few drops of $K_2Cr_2O_7$ or of K_2CrO_4 solution. Stir the mixture carefully. Explain the colour of the ether layer, the gradually changing colour of the aqueous phase and the liberation of gas.

31. How does the chemical nature of similar compounds change with the increasing oxidation state of chromium in the series CrO-Cr_2O_3-CrO_3; $Cr(OH)_2$-$Cr(OH)_3$-H_2CrO_4; CrF_2-CrF_3-CrF_6? Illustrate your answer by examples of reactions.

32. Explain the following observations and write the reaction equations.

When alkali is added to a solution of a chromium(III) compound a grey-blue substance precipitates. Excess alkali dissolves it and the solution turns green. Add bromine to the green solution and heat: the solution turns yellow.

Add dilute acid to the yellow solution: the colour changes to orange. Add hydrogen sulphide water: the solution turns green again and precipitates a yellow substance. Separate the precipitate on a filter and add acid and metallic zinc granules (without access of air): the solution turns blue. On exposure to air, the green colour of the solution is gradually restored.

33. Explain the industrial processes used to obtain $K_2Cr_2O_7$ and illustrate your explanations with reaction equations.

Fuse chromite with soda at 1000-1300°C in the air. Leach the obtained brown-yellow material: a yellow solution is formed. Add acid: the solution turns orange. Cool the solution and add potassium chloride: orange-red crystals precipitate.

11.5. Compounds of Cr(0), Mo(0) and W(0)

34. (a) Explain the following experimental facts.

Chromium hexacarbonyl is a diamagnetic compound; its molecule is octahedral with the chromium atom in the centre; the electric charge on the chromium atom is 0.4 + of the absolute charge of the electron.

(b) What is the practical importance of carbonyls of chromium, molybdenum and tungsten?

CHAPTER 12

d-Elements of Group VII

12.1. Elements and Simple Substances

1. Construct graphs showing the variation of the atomic and ionic radii, ionization energy with the atomic number of the elements in the manganese subgroup.

(a) Explain the curves.

(b) What oxidation states are the most characteristic of manganese, technetium and rhenium?

(c) In the form of what ions do Mn(II), Mn(IV), Mn(VI), Mn(VII) and Re(VII) exist in aqueous solution?

2. Explain the variations in the melting points, heats of fusion and sublimation of metals in the series Mn-Tc-Re.

3. Give equations of the corresponding half-reactions and standard oxidation-reduction potentials E° in an acid medium for the systems Mn^{2+}/Mn, TcO_4^-/Tc, and ReO_4^-/Re.

(a) How does the chemical activity change in the series Mn-Tc-Re?

(b) What is the attitude of the metals to hydrochloric, dilute

sulphuric and concentrated nitric acids? Write reaction equations.

(c) What volume of concentrated HNO_3 (density 1.5) is required to dissolve 10 g of rhenium?

Experiment 1. The attitude of manganese and rhenium to dilute acids. Study the attitude of manganese and rhenium to hydrochloric and dilute sulphuric acids.

4. (a) What simple substances (see Fig. 75) are suitable for the reduction of Mn_3O_4 and TcO_2 to metals?

(b) What methods are used to obtain manganese and ferromanganese in industry?

(c) By what reaction is rhenium obtained?

Experiment 2. Obtaining manganese by aluminothermy. Prepare Mn_3O_4. To that end, place 40 g of powdered MnO_2 into a crucible and heat at 800°C in a muffle furnace for an hour. Cool the obtained Mn_3O_4, grind to powder and mix thoroughly with 10 g of aluminium powder. Place the mixture into a chamotte crucible and cover with a layer of 10 g of the ignition mixture*. Insert a magnesium ribbon into the mixture. Place the crucible into the hood, light the magnesium by a burning splint fixed in a long glass tube. Explain the active course of the reaction. When the mass is cooled, separate the metal from slag and hand over to the laboratory assistant.

5. What processes occur at the carbon electrodes during the electrolysis of a manganese(II) sulphate solution?

Experiment 3. Obtaining manganese by electrolysis. Place an electrolyte containing 120 g of $MnSO_4 \cdot 6H_2O$ and 125 g of $(NH_4)_2SO_4$ per litre of water into an electrolyzer with carbon electrodes. Pass current for 30 minutes, the cathode density of the current being 4 A/dm^2. Next remove the cathode from the solution, rinse with water and dry with filter paper. Dissolve the obtained manganese in concentrated nitric acid. Wash the electrode.

12.2. Compounds of Mn(II)

6. (a) What is the electron configuration of the Mn^{2+} ion and what coordination number is the most characteristic of Mn(II) in compounds?

(b) What is the structure of the following crystals: MnO, MnS, MnF_2 and $MnCl_2$, $Mn(OH)_2$?

7. Give the electron configuration of octahedral aquo, fluorine, thiocyanate, chlorine, and cyanocomplexes of manganese II.

(a) Which of these are low-spin and which are high-spin complexes?

(b) Write equations for the formation of the complexes mentioned. How do they act in dilute solutions?

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* The ignition mixture consists of powdered BaO_2 and Mg (3 : 1). Prepare the mixture by shaking the powders in a bottle. Never grind the ingredients in a mortar!

8. (a) What complexes (cation aquo complexes or anion hydroxy complexes) are the most characteristic of the 3*d*-elements in the +2 oxidation state in water solutions?

(b) What are the unit cells of the crystals: $Mn(NO_3)_2 \cdot 6H_2O$, $Mn(ClO_4)_2 \cdot 6H_2O$, $MnSO_4 \cdot 4H_2O$?

Experiment 4. Obtaining manganese(II) hydroxide and its properties. Obtain $Mn(OH)_2$ by an exchange reaction. Note its colour.

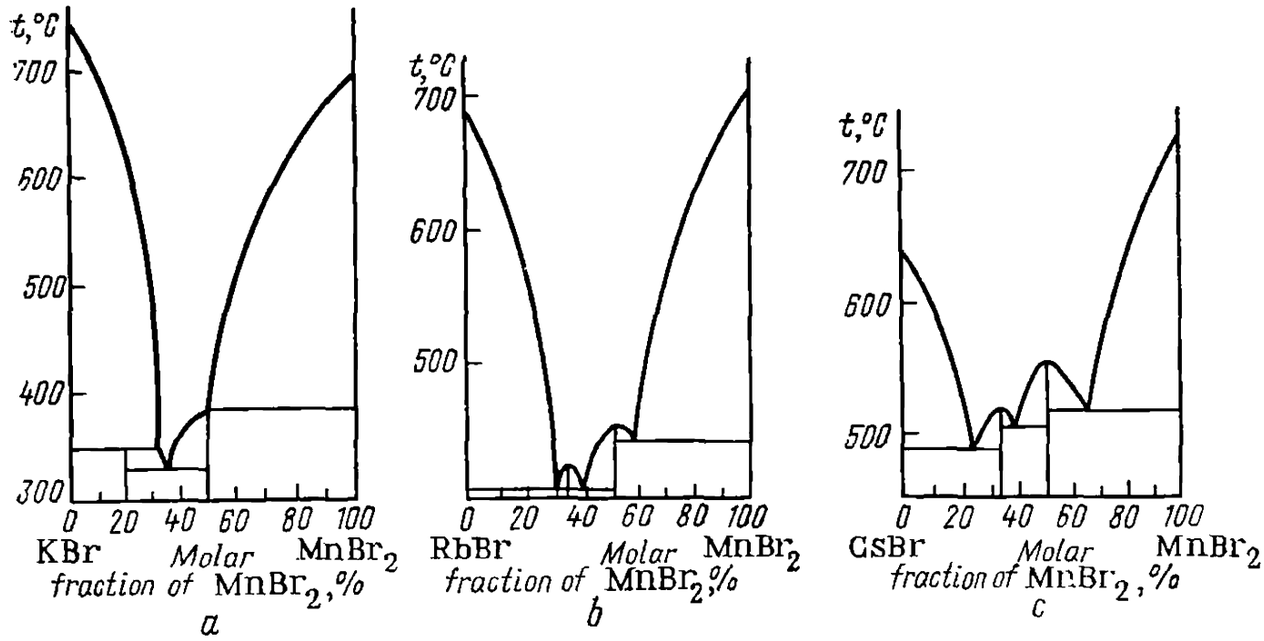


Fig. 80. Phase diagrams of the systems $KBr\text{-}MnBr_2$ (*a*), $RbBr\text{-}MnBr_2$ (*b*) and $CsBr\text{-}MnBr_2$ (*c*)

Divide the precipitate into two parts and try the attitude of one part of the precipitate to acids and alkalis. Stir the other part with a glass rod. Explain your observations.

Experiment 5. Obtaining crystal hydrate $Mn(NO_3)_2 \cdot 6H_2O$. (Use the hood!) Calculate the amounts of the starting components to obtain the required quantity of $Mn(NO_3)_2 \cdot 6H_2O$ by an exchange reaction between $MnCO_3$ and 30-35 per cent HNO_3. Place, while stirring, excess manganese(II) carbonate into a porcelain dish or a beaker containing the calculated quantity of 30-35 per cent nitric acid. The last portion of manganese(II) carbonate should remain undissolved. Separate the precipitate from the solution of manganese(II) nitrate by filtration and acidify the solution with nitric acid to a weak acid reaction. Evaporate the solution on a water bath (at 60-65°C) until its sample precipitates crystals on cooling. Cool the solution. Separate the crystals on a Schott funnel with suction and transfer into a bottle provided with a ground-in stopper. Describe the appearance of the crystals.

9. How will the pH change if Mn(II) salts are dissolved in water? Write equations of hydrolysis of manganese(II) compounds.

Experiment 6. Hydrolysis of manganese(II) salts. Determine the medium of Mn(II) salt solution. Write reaction equations.

10. The results of thermal analysis of the system manganese dibromide-alkali metal bromide are given in Fig. 80.

(a) What compounds are formed in these systems and how does their stability change with the increasing atomic number of the alkali metal?

(b) How do manganate(II) halide crystals interact with water? Write the equation of the reaction that occurs when the solution is diluted.

11. A very sensitive reaction for detection of manganese(II) compounds is based on the oxidation of Mn(II) derivatives with formation of a violet ion MnO_4^-.

(a) Can ammonium persulphate be used as an oxidant in this reaction?

(b) Can concentrated hydrochloric acid be used to create the desired medium? To prove your answer give E°_{298} of the corresponding systems.

Experiment 7. Formation of the MnO_4^- ion. (Test for the Mn^{2+} ion.) Add 2-3 drops of $AgNO_3$ solution and dilute $Mn(NO_3)_2$ solution to ammonium persulphate solution in a test tube. Heat the mixture. Explain your observations (the Ag^+ ion acts as a catalyst).

12.3. Compounds of Mn(IV), Tc(IV) and Re(IV)

12. Give the electron configuration of the octahedral complexes MnF_6^{2-}, $[MnF_5(OH)_2)]^-$, $[MnI_6]^{2-}$.

(a) Why is the coordination number 6 most characteristic of the complexing agent with the electron configuration of $3d^3$?

(b) What is the structure type of MnO_2?

13. Write equations for reactions of MnO_2 with CaO and H_2SO_4; of $TcCl_4$ with KCl; of $ReBr_4$ with KBr.

14. Under what conditions can Mn(IV) compounds be converted to derivatives of Mn(II) and Mn(VI)? Give examples of reactions.

12.4. Compounds of Mn(VI), Tc(VI) and Re(VI)

15. Give examples of binary compounds and the corresponding complexes of Mn(VI), Tc(VI) and Re(VI).

(a) What element of the manganese subgroup is most characterized by the +6 oxidation state?

(b) What ligands stabilize the +6 oxidation state?

(c) The hexafluorides TcF_6 (m.p. 33.4°C, b.p. 55.3°C) and ReF_6 (m.p. 18.8°C, b.p. 47.6°C) melt and boil at low temperatures and sublime easily. Explain this fact.

(d) Why is the melting point of ReO_3 (160°C) higher than that of ReF_6?

16. Characterize the acid-base properties of binary and ternary compounds of E(VI).

(a) Write equations for reactions of ReO_3 with KOH, of TcF_6 and ReF_6 with H_2O, of $ReOF_4$ and TcF_6 with KF.

(b) What type of oxidation-reduction process accompanies hydrolysis of E(VI) compounds?

17. Under what conditions can oxymanganates(VI) be obtained from compounds of Mn(II), Mn(IV) and Mn(VII)? Give reaction equations.

18. The MnO_4^{2-} ion can be expected to show both oxidizing or reducing properties associated with the decreasing or increasing oxidation state of manganese. Under what conditions does the MnO_4^{2-} ion transform into Mn^{2+}, MnO_2 and MnO_4^-? Give reaction equations.

Experiment 8. Obtaining potassium tetraoxymanganate(VI). Fuse a pinch of $KClO_3$ with a lump of KOH and a few grains of MnO_2. Keep the melt in the test tube (for use in future experiments). Write the reaction equation.

Experiment 9. Oxidizing properties of the MnO_4^{2-} ion. (a) Add by drops K_2MnO_4 solution to $FeSO_4$ solution acidified with sulphuric acid.

(b) Add Na_2SO_3 solution to K_2MnO_4 solution and heat slightly. Explain the reactions.

Experiment 10. Reducing properties of the MnO_4^{2-} ion. Add chlorine water to K_2MnO_4 solution. Explain your observations.

Experiment 11. Disproportionation of the MnO_4^{2-} ion. Add a few drops of acetic acid to K_2MnO_4 solution. Explain the colour of the resultant solution and the precipitation.

12.5. Compounds of Mn(VII), Tc(VII) and Re(VII)

19. Give examples of compounds of manganese(VII), technetium(VII) and rhenium(VII) and their anion complexes.

(a) What is the structure of Mn_2O_7 and of MnO_3F and how does it agree with their low melting points (m.p. of Mn_2O_7 is 6°C, m.p. of MnO_3F is −38°C)?

(b) What are the acid-base properties of binary and ternary compounds of E(VII)? Give examples of reactions of E_2O_7 and EO_3F with H_2O, of Re_2S_7 with K_2S.

20. Figure 81 shows the absorption spectrum of the MnO_4^- ion. What is the wavelength of the absorption maximum? What is the colour of the absorbed radiation and how does it agree with the colour of the MnO_4^- ion?

21. Suggest two methods of obtaining $KMnO_4$ from MnO_2 incorporating the following stages of transformation: Mn(IV) → Mn(VI) → → Mn(VII).

Experiment 12. Synthesis of potassium tetraoxymanganate(VII). (Use the hood. Wear goggles!) Fuse calculated amounts of potassium hydroxide and potassium chlorate(V) in an iron crucible using a blow lamp. Stop heating, stir the melt with an iron wire and add, by small portions, fine powder of manganese dioxide. (Manganese

dioxide should be free from organic impurities since they form an explosive mixture with potassium chlorate.) Heat the reaction mixture to the temperature of red heat. Cool the crucible and place it in water in a porcelain dish. When the melt separates from the crucible, dissolve it in water. Boil the solution and pass the current of carbon dioxide into the boiling solution until a drop of the solution colours a filter paper crimson. (Green shades due to K_2MnO_4 should not be present.)

Cool the solution, pass it through a glass filter, evaporate on a water bath until crystallization begins, and cool. Separate the crystals on a Schott funnel with suction, and dry.

22. $KMnO_4$ decomposes at 250°C; $KTcO_4$ melts at 540°C and $KReO_4$ at 550°C; they sublime without decomposition at 1000°C.

(a) Explain the changing stability in the series $KMnO_4$-$KTcO_4$-$KReO_4$.

(b) Write the equation for thermal decomposition of potassium tetraoxymanganate(VII) ($\Delta H < 0$). Can this reaction be reversed?

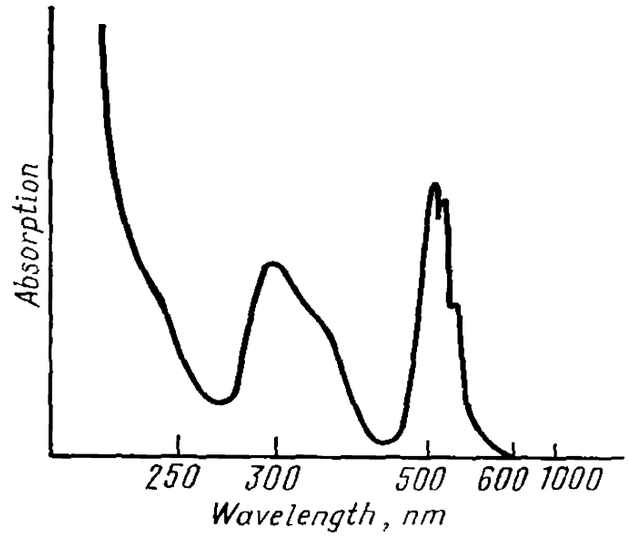


Fig. 81. Absorption spectrum of the MnO_4^- ion

Experiment 13. Thermal decomposition of $KMnO_4$. Heat $KMnO_4$ crystals in a test tube over a burner. Identify the evolving gas. Cool the test tube and dissolve the solid product in an alkali solution. Separate the solution from the precipitate by decantation or filtration and add acetic acid. Explain the changing colour of the solution and precipitation.

23. Unlike $KMnO_4$, which is sufficiently stable, $HMnO_4$ has not been isolated in the free state. An attempt to obtain it by an exchange reaction gives Mn_2O_7. Mn_2O_7, in turn, is markedly less stable than $KMnO_4$ and decomposes with an explosion. Explain these experimental facts.

24. (a) Using the tabulated standard oxidation-reduction potentials of the corresponding systems, decide whether or not a reaction will occur between an acidified solution of $KMnO_4$ and Na_2SO_3 solution; $KMnO_4$ solution and Na_2SO_3 solution; strongly alkaline $KMnO_4$ solution and a large excess of Na_2SO_3 solution.

(b) What medium favours the transition of MnO_4^- to $Mn(OH_2)_6^{2+}$, MnO_4^- to MnO_2 and MnO_4^- to MnO_4^{2-}?

(c) In what medium (acid or alkaline) are the oxidizing properties of the MnO_4^- ion the strongest? Explain your answer.

(d) What is the role of the medium (of the H^+ and OH^- ions, H_2O molecules) in the activation of the MnO_4^- ion?

Experiment 14. Effect of medium on the oxidizing properties of the MnO_4^- ion. Add dilute acid, water and concentrated alkali solution into three separate test tubes containing dilute $KMnO_4$ solution. Note the colour of the solutions. Add Na_2SO_3 solution to the test tubes. (Add a large excess of Na_2SO_3 solution to the alkaline solution of $KMnO_4$). Explain your observations.

Experiment 15. Oxidizing Mn(II) derivatives by the MnO_4^- ion. Add $MnSO_4$ solution to a strongly dilute $KMnO_4$ solution. Explain your observations.

Experiment 16. The oxidizing properties of manganese(VII) oxide. (Use the hood. Half-close the screen!) Place a few crystals of $KMnO_4$ on a watch glass, carefully add a few drops of concentrated sulphuric acid and stir with a glass rod. Place a small quantity of the mixture into a porcelain dish on a piece of cotton wool moistened slightly with alcohol. Observe the inflammation of alcohol. Never use the same glass rod again if the experiment is repeated, and take a new one instead.

25. Distribute valency electrons in the molecular orbitals of tetrahedral oxyanions of Mn(VII), Mn(VI) and Mn(V).

(a) How does the share of π-bonding in EO_4^{n-} change with the increasing oxidation state of manganese?

(b) Compare the stability of the ions with the frequency of valency oscillations of Mn—O bonds and with the parameters of splitting of oxyanions Δ:

	MnO_4^-	MnO_4^{2-}	MnO_4^{3-}
$\tilde{\nu}$, cm^{-1}	905	885	792
Δ, cm^{-1}	26,000	19,000	11,000

26. How does the chemical nature of similar compounds change with the increasing oxidation state of manganese in the series MnO-Mn_2O_3-MnO_2-MnO_3-Mn_2O_7; $Mn(OH)_2$-$Mn(OH)_3$-$Mn(OH)_4$-$HMnO_4$?

27. Give ΔG_f° of E_2O_7 and EO_4^-. Explain the similarity of many properties of technetium and rhenium compounds and their difference from those of manganese compounds.

12.6. Cluster Compounds

28. The chemical analysis of manganese carbonyl reveals the composition of $Mn(CO)_5$. This compound is diamagnetic. The measurement of its molecular mass shows that its molecule is dimeric. There are three lines of absorption at 2068, 2039 and 2006 cm^{-1} (corresponding to the valency oscillations of the terminal groups) in the infrared spectrum of manganese (Fig. 82). Absorption at frequencies below 1900 cm^{-1} (1785-1875 cm^{-1}), which is characteristic of bridge CO-groups, is not revealed in the spectrum.

(a) Using these data, draw your conclusion on the structure of the molecule of manganese carbonyl. Write its structural formula.

(b) What manganese (0) orbitals account for the chemical bond in the carbonyl molecule?

(c) What compounds of Tc(0) and Re(0) are known?

29. $K_2Re_2Cl_8 \cdot 2H_2O$ can be obtained by reducing $KReO_4$ with hydrogen or with H_3PO_2 in HCl solution.

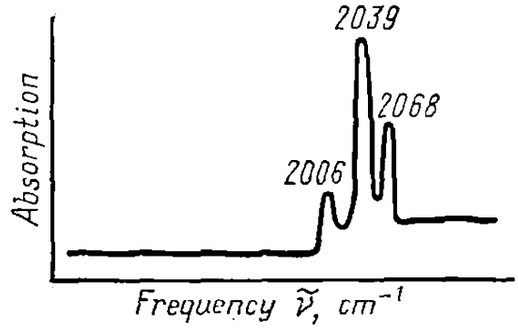


Fig. 82. The I-R spectrum of $Mn_2(CO)_{10}$ in the gaseous phase in the regions of valency oscillation of the CO-group

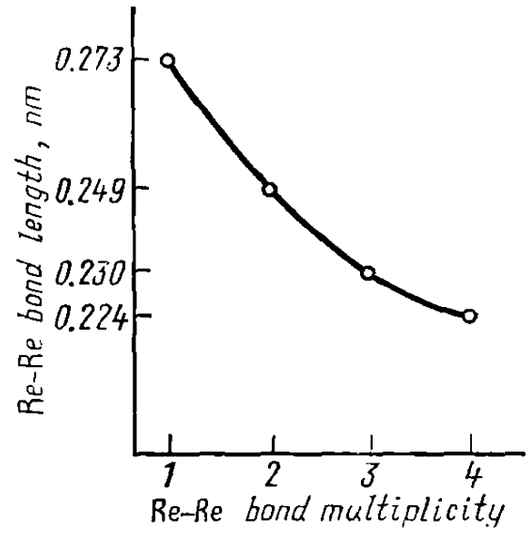


Fig. 83. Dependence between multiplicity and bond length Re—Re

(a) Explain the structure of the $Re_2Cl_8^{2-}$ ion assuming that it is diamagnetic and its internuclear distance Re-Re is 0.224 nm (Fig. 83).

(b) What rhenium(III) orbitals are involved in the formation of bonds in the $Re_2Cl_8^{2-}$ complex?

30. The diamagnetic molecule of rhenium trichloride is a trimer Re_3Cl_9. The internuclear distance Re—Re is 0.249 nm which is 0.027 nm shorter than in rhenium metal.

(a) What is the multiplicity of the Re—Re bond in the Re_3Cl_9 molecule (Fig. 83)?

(b) What rhenium orbitals account for chemical bonding in this compound?

(c) Why can the diamagnetic compounds $Rb_3[Re_3Cl_{12}]$, $Rb_2[Re_3Cl_{11}]$ and $Rb[Re_3Cl_{10}]$ be obtained from the reaction of RbCl with Re_3Cl_9 in concentrated HCl? The internuclear distance Re—Re in the $Re_3Cl_{12}^{3-}$, $Re_3Cl_{11}^{2-}$ and $Re_3Cl_{10}^{-}$ ions is 0.249 nm.

CHAPTER 13

d-Elements of Group VIII.

The Iron Subgroup

13.1. Elements and Simple Substances

1. (a) Analyse (preferably graphically) and explain the variations of the atomic and ionic radii and ionization energy in the series Fe-Ru-Os.

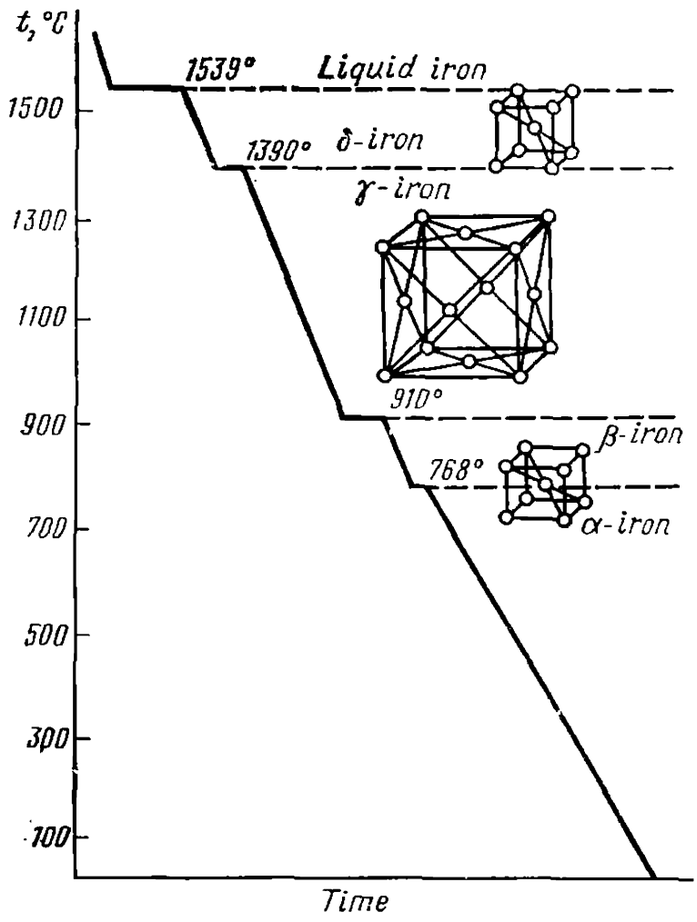


Fig. 84. Iron cooling curve

(b) What oxidation states are most characteristic of Fe, Ru and Os?

2. (a) Explain the character of variation of the melting point, heats of fusion and sublimation in the series Fe-Ru-Os.

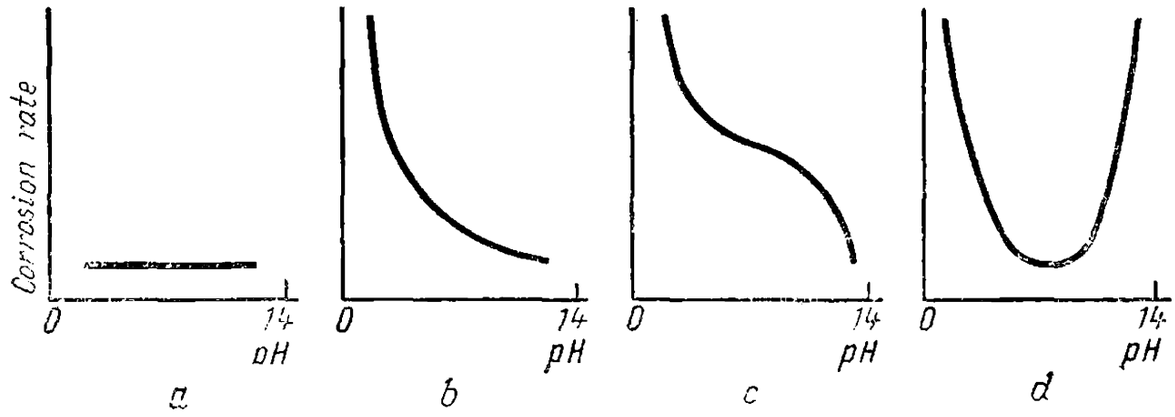


Fig. 85. Typical curves showing the variation of metal corrosion rate with pH

(b) How does the electrode potential of the E^{2+}/E system change in transition from iron to osmium? Explain your answer.

3. Figure 84 shows the curve describing the process of iron cooling. What processes are described by the level parts of the curve?

4. Figure 85 shows typical curves describing the dependence of

corrosion on the pH of the medium. What regularities can be found in the corrosion destruction of iron, ruthenium and osmium?

Experiment 1. Reaction of iron, ruthenium and osmium with water, acid and alkali. Study the reactions of the metals with alkalis and acids.

5. Explain the dependence of the dissolution rate of iron in sulphuric acid on the acid concentration (Fig. 86). What causes passivation of metals?

Experiment 2. Passivating iron. Grind two iron plates with abrasive paper, degrease them in concentrated hydrochloric acid, wash with water and dry in filter paper. Immerse one plate into concentrated nitric or sulphuric acid for 1-2 minutes. Carefully extract the plate from the acid and wash with water. Now immerse both plates into copper(II) sulphate solution. Explain the different attitude of the iron plates to $CuSO_4$ solution.

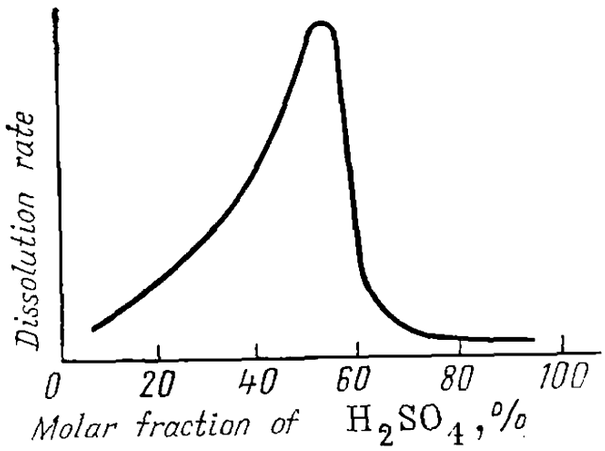


Fig. 86. Effect of sulphuric acid concentration on the rate of iron dissolution

6. Write equations of the reactions that occur during corrosion of zinc- and tin-plated iron.

Experiment 3. Corrosion of zinc- and tin-plated iron. Grind two iron wires with abrasive paper. Attach a thin tin plate to one and zinc plate to the other wire. Immerse the wires into two separate test tubes filled with water acidified with a few drops of dilute sulphuric acid. Add two drops of a solution of $K_3[Fe(CN)_6]$ into each test tube. Blue colour develops in one test tube sooner than in the other. Explain.

7. Figure 87 shows the variation of ΔG_f° of oxides with temperature.

(a) At what temperature is the reduction of iron oxide with carbon and carbon monoxide thermodynamically probable?

(b) What chemical reactions occur in the blast furnace process?

(c) Describe the methods for obtaining iron of special purity.

Experiment 4. Obtaining pyrophoric iron and its properties. Place dry powder of ferrous oxalate, $Fe(COO)_2$, into a dry test tube and fix it in the inclined position. Heat over a burner (Fe_3O_4 can be formed with strong heating). The reaction is complete when gas stops evolving and black powder is formed. Remove moisture drops from the walls of the test tube with filter paper. Stopper the test tube and cool. Put the obtained powder on asbestos net. Explain your observations.

Experiment 5. Obtaining iron by electrolysis. Carry out the experiment as instructed for obtaining manganese(II) sulphate by electrolysis. The electrolyte contains 75 g of $FeCl_2 \cdot 4H_2O$, 150 g of

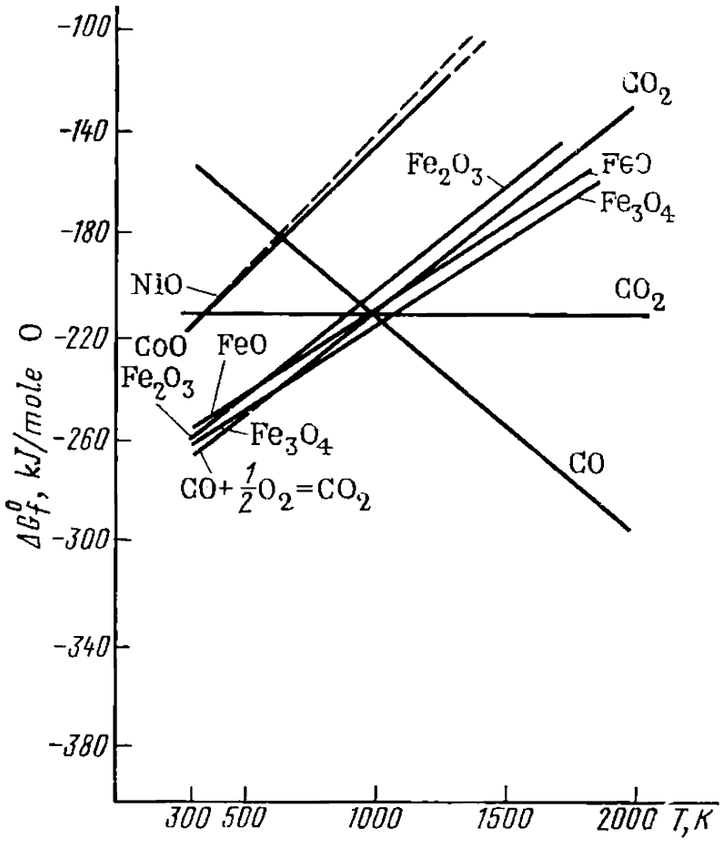


Fig. 87. Variation of ΔG_f° of some oxides of *d*-elements of group VIII with temperature (for the legend see Fig. 21)

$FeSO_4 \cdot 7H_2O$, 120 g of $(NH_4)_2SO_4$ and 8 g of $(NH_4)_2C_2O_4$ per litre of water. The cathode density of current, 1 A/dm^2.

8. The following experimental data are known. α-Iron reacts with vanadium and chromium to give continuous solid solutions. Iron does not react with calcium or potassium. Iron forms various compounds with titanium and aluminium.

(a) Explain these facts.

(b) Give examples of iron alloys characterized by high corrosion resistance, refractoriness and increased hardness.

13.2. Compounds of Fe(0), Ru(0) and Os(0)

9. Iron carbonyl, $Fe(CO)_5$, is diamagnetic. It melts at low temperature (—20°C) and boils at 103°C. Readily soluble in organic solvents.

(a) Explain the structure of this compound.

(b) Write the equation of the reaction of iron pentacarbonyl with iodine, sodium (in liquid ammonia) and alkali. Characterize the attitude of $Fe(CO)_5$ to ultraviolet radiation.

10. The I-R spectrum of the $Fe_2(CO)_9$ molecule has absorption bands at 2082 and 2019 cm^{-1} belonging to the terminal CO-groups and a band at 1829 cm^{-1} corresponding to the bridge CO-groups.

(a) What is the structure of the $Fe_2(CO)_9$ molecule if the coordination number of iron is 6?

(b) Why is the oscillation frequency of the terminal CO-groups higher than that of the bridge CO-groups?

(c) Why is the order of the CO-bond in the tetrahedral complex $Fe(CO)_4^{2-}$ lower ($n_{CO} = 1.85$) than in the CO-molecule ($n_{CO} = 3$)?

13.3. Compounds of Fe(II)

11. What is the most characteristic coordination number of Fe(II)?

(a) Describe the structure of crystals of FeO, FeF_2 and $FeCl_2$, $Fe(OH)_2$.

(b) Explain the great difference between the melting points of FeF_2 (1100°C) and $FeCl_2$ (667°C).

(c) Why do MnO and FeO, $MnCl_2$ and $FeCl_2$ form continuous solid solutions while $FeCl_2$ and $CuCl_2$ form eutectics?

12. Give the electron configuration of aquo, ammino, fluorine, chlorine, bromine, cyan complexes of iron(II). Which of these are high-spin, low-spin, dia- and paramagnetic complexes?

13. X-Ray structural analysis shows that the crystals of Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, have an insular ionic lattice. This compound is paramagnetic. What ions compose the crystal of Mohr's salt?

Experiment 7. Synthesis of Mohr's salt. Dissolve a mixture of crystals of $FeSO_4 \cdot 7H_2O$ and of $(NH_4)_2SO_4$ (2 : 1) in the minimum water. (At 80°C, 94.1 g of $(NH_4)_2SO_4$ and 43.7 g of $FeSO_4$ dissolve in 100 g of water.) Filter the solutions if necessary, heat to 60-70°C, pour into a porcelain dish, acidify with dilute sulphuric acid and cool while stirring with a glass rod. Separate the precipitated crystals on a Büchner funnel and dry at 50-60°C. Test the crystals for the presence of the NH_4^+, Fe^{2+} and SO_4^{2-} ions.

14. Characterize the oxidation-reduction properties of Fe(II) compounds.

(a) Why does the colour of many ferrous compounds (especially in solution form) change on exposure to air? (For example, a solution of $Fe(OH)_2$ quickly turns brown in air.)

(b) What reaction occurs between acidified solutions of $FeSO_4$ and $KMnO_4$?

To prove your answer give the oxidation-reduction potentials of the corresponding systems.

Experiment 8. Reducing properties of iron(II) compounds. Add solutions of $KMnO_4$ and $K_2Cr_2O_7$ into two separate test tubes containing a solution of an iron(II) compound acidified with dilute sulphuric acid. Explain your observations.

Experiment 9. Iron(II) hydroxide and its properties. Obtain $Fe(OH)_2$ by an exchange reaction using solutions free of dissolved oxygen. (Use freshly boiled water to prepare such solutions. Boil the obtained solutions. Wear goggles to protect the eyes from splashing of the alkali.) Use part of the precipitate to determine the acid-base prop-

erties of the hydroxide. Keep the remaining part in the air. Explain your observations.

15. What iron sulphide (FeS or FeS_2) is more likely to be formed by the reaction of the simple substances under normal conditions? To prove your answer give ΔG_f° of these sulphides with reference to one mole of S.

Experiment 10. Obtaining iron(II) sulphide by the reaction between the simple substances. (Use the hood!) (a) Thoroughly mix powders of reduced iron and sulphur flowers (6 : 4) in a porcelain mortar using a pestle. Place a part of the mixture on a sheet of asbestos, heat a glass rod in the flame of a burner, and touch the mixture with the rod. Observe spontaneous heating of the mixture. Try the obtained product with hydrochloric acid.

(b) Place an equivalent mixture of sulphur and iron in a crucible and add a few drops of water. Mix the mass into a thick paste. Observe the volcanic reaction (spontaneous heating, liberation of steam).

16. Can ferrous sulphide be obtained by a reaction between a solution of an iron(II) compound with hydrogen sulphide solution? In your answer use the result of Experiment 10,a.

Experiment 11. Obtaining iron(II) sulphide in solution. Check experimentally if it is possible to obtain iron(II) sulphide by a reaction between $FeSO_4$ solution and a solution of: (a) hydrogen sulphide and (b) ammonium sulphide. Act with hydrochloric acid on the precipitated ferrous sulphide. Explain your observations.

13.4. Compounds of Fe(III)

17. What is the most characteristic coordination number of Fe(III) in compounds? Describe the structure of FeF_3, Fe_2O_3 and $FeCl_3$. Compare the melting points of FeF_3 and $FeCl_3$.

18. (a) In what form does the Fe^{3+} ion exist in acid and strong alkaline solutions? Write equations of reactions illustrating the acid-base properties of ferric hydroxide.

(b) Give examples of ferrites of the salt and mixed oxide type.

Experiment 12. Iron(III) hydroxide. Study the acid-base properties of freshly obtained iron(III) hydroxide. Act with a concentrated solution of alkali on a small quantity of the hydroxide and heat for a long time (test for acid properties).

Experiment 13. Iron(III) oxide. (Use the hood!) Obtain iron(III) oxide, Fe_2O_3, by thermal decomposition of $Fe(NO_3)_2 \cdot 6H_2O$. To that end, calcine the crystals of $Fe(NO_3)_2 \cdot 6H_2O$ in a porcelain crucible until gas stops evolving. Write the reaction equation.

(a) Use a part of the oxide to study its reaction with dilute sulphuric acid and alkali solution.

(b) Melt $Na_2CO_3 \cdot 10H_2O$ in a porcelain crucible. Place Fe_2O_3 into the melt. Observe the evolution of gas and formation of a yellow

melt. Cool the melt and act on it with water. Explain your observations.

19. Write the equation of hydrolysis of $Fe(OH_2)_6^{3+}$.

(a) What reactions occur when the solution is heated or when its pH is lowered or raised?

(b) Why is ferric hydroxide of variable composition?

Experiment 14. Hydrolysis of iron(III) salts. (a) Dissolve crystals of $Fe(NO_3)_3 \cdot 6H_2O$ ($KFe(SO_4)_2 \cdot 12H_2O$) in water. Note the colour of the solution and measure its pH. Place the solution into three test tubes. Add dilute H_2SO_4 to the first of them, alkali solution to the second and heat the third. Explain your observations.

(b) Add a soda solution to a solution of an iron(III) salt. Explain your observations.

20. (a) Give the electron configuration of the aquo, ammino, fluorine, chlorine, and cyan complexes of iron(III).

(b) What complexes are they: high- or low-spin, para- or diamagnetic?

(c) Write equations of reactions of their formation.

21. Write overall constants of stability of the following complexes: $Fe(CNS)_6^{3-}$, FeF_6^{3-}, $Fe(CN)_6^{3-}$.

(a) Which of these complexes has the highest stability? Explain your answer.

(b) What is the colour of $Fe(CNS)_6^{3-}$ if it absorbs maximum at 480-490 nm?

(c) Will the colour of the solution containing the ions Fe^{3+} and CNS^- persist if solutions of NaF, KCN or Na_3PO_4 are added to it? Check your answer by carrying out the following experiments.

Experiment 15. Comparing stability of thiocyanate, fluoride, and cyanide complexes of iron(III). (a) Add a few drops of potassium thiocyanate or ammonium thiocyanade to a ferric salt solution. Add sodium fluoride to the obtained solution. Explain your observations.

(b) Add potassium (or ammonium) thiocyanate solution to potassium hexacyanoferrate(III) solution. Explain why the solution colour persists.

Experiment 16. Obtaining chlorine complexes of iron(III). Add concentrated hydrochloric acid to ferric chloride until the colour changes. Dilute the solution with water. Explain your observations.

22. What type of compounds (salts or mixed cyanides) are hexacyanoferrates(III) of *d*-elements and what is their solubility?

Experiment 17. Using potassium ferricyanide, $K_3[Fe(CN)_6]$, and potassium ferrocyanide, $K_4[Fe(CN)_6]$ in chemical analysis. Qualitative tests for Fe^{2+} and Fe^{3+} ions. (a) Add $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ into two separate test tubes containing freshly obtained $FeSO_4$ solution. Note in which of them the colour of the solution changes. Explain your observations.

(b) Add solutions of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ to two separate test tubes containing a solution of an iron(III) salt. Note in which test tube the solution colour changes. Explain.

23. Can ferric halides be obtained in solution by exchange reactions? To prove your answer compare E°_{298} of the corresponding systems.

Experiment 18. Oxidizing properties of iron(III) compounds. To reveal the oxidizing properties of iron(III) derivatives in acid medium carry out the corresponding reactions using the solutions of KI and H_2S as reductants. Explain.

13.5. Compounds of Fe(VI), Ru(VI) and Os(VI)

24. Give examples of compounds in which the oxidation state of iron, ruthenium and osmium is +6.

(a) Give the electron configuration of the FeO_4^{2-} tetrahedral ion. What is the role of π-bonding in the stabilization of this ion?

(b) Under what conditions can Fe, Fe_2O_3, $FeCl_3$ be converted into the FeO_4^{2-} ion? Write reaction equations.

(c) What are the oxidizing-reducing properties of the FeO_4^{2-} ion and how does its stability depend on pH?

25. Absorption bands at 510 and 787 nm are found in the spectrum of FeO_4^{2-}. What is the colour of this ion?

26. Oxyferrates(VI) are isostructural to oxysulphates(VI) and oxychromates(VI) and form solid solutions with them. Draw your own conclusion on the solubility of $BaFeO_4$ and K_2FeO_4.

Experiment 19. Obtaining oxyferrates(VI) and their properties. (Use the hood!) Add 3-5 drops of liquid bromine and a small amount of $FeCl_3$ solution to ground potassium hydroxide in a porcelain dish. Heat the mixture until a violet-red compound is formed. Dissolve the product in water. React the obtained solution with $BaCl_2$ solution, with dilute sulphuric acid and with hydrogen sulphide water. Explain your observations.

13.6. Compounds of Ru(VIII) and Os(VIII)

27. Give examples of compounds of Ru(VIII) and Os(VIII) and the corresponding complexes.

(a) Describe the structure and electron configuration of EO_4 molecules.

(b) What molecule, RuO_4 (k = 672 N/m, ΔH_f° = −184.1 kJ/mole) or OsO_4 (k = 800 N/m, ΔH_f° = −336.4 kJ/mole) is more stable and why?

(c) Why do RuO_4 and OsO_4 melt and boil at low temperatures? Why are they highly volatile?

28. Give examples of reactions illustrating the acid-base properties of tetraoxides of ruthenium and osmium.

CHAPTER 14

d-Elements of Group VIII.

The Cobalt Subgroup

14.1. Elements and Simple Substances

1. (a) Analyse (preferably graphically) and explain the character of variation of atomic and ionic radii, ionization energy with the atomic number of the elements in the subgroup.

(b) What oxidation states are inherent in the elements and how does the characteristic oxidation state change in the series Co-Rh-Ir?

2. (a) Explain the character of variation of the melting point, enthalpy of fusion and sublimation of metals in the series Co-Rh-Ir.

(b) How does the electrode potential E^{2+}/E change in transition from Co to Ir?

3. (a) What methods are used to obtain cobalt?

(b) Which simple substances (of those given in Fig. 87) can reduce Co_3O_4 to pure metal?

(c) What reactions occur at graphite electrodes during the electrolysis of cobalt(II) sulphate solution?

Experiment 1. Obtaining cobalt by electrolysis. (Use the hood!) The composition of the electrolyte in the electrolyzer is as follows: 120 g of $CoSO_4 \cdot 7H_2O$ and 55 g of $(NH_4)_2SO_4$ per litre of water. Carry out electrolysis at the cathode density of current of 2 A/dm^2 for 30 minutes. Then remove the cathode from the solution, rinse with distilled water and dry in filter paper.

Test the attitude of the metal to sulphuric, hydrochloric and nitric acid. Remove the deposited metal from the electrode by dissolving it in concentrated nitric acid. Wash the electrode thoroughly.

14.2. Compounds of Co(0), Rh(0) and Ir(0)

4. Experiments show that cobalt carbonyl, $Co_2(CO)_8$, melts at low temperature (51°C), is insoluble in water but readily soluble in organic solvents; decomposes at 60°C. The compound is diamagnetic. Its I-R spectrum has absorption bands at 2077, 2054 and 2034 cm^{-1} (which correspond to the terminal CO-groups) and at 1859 cm^{-1} (bridge CO-groups). The coordination number of Co in the carbonyl is 6.

(a) Once this is known, what is the structure of cobalt octacarbonyl?

(b) Describe the conditions for obtaining $Co_2(CO)_8$ and its uses.

(c) Give examples of rhodium(0) and iridium(0) compounds.

14.3. Compounds of Co(II)

5. (a) What are the most characteristic coordination numbers of Co(II)?

(b) Characterize the magnetic properties of octahedral aquo, ammino, fluoride and chlorine complexes of Co(II).

(c) Describe the structure of CoO, CoF_2 and $Co(OH)_2$, $CoCl_2$, $CoCO_3 \cdot 6H_2O$ and $CoCl_2 \cdot 2H_2O$. Why do the melting points of CoF_2 (1200°C) and $CoCl_2$ (740°C) differ greatly?

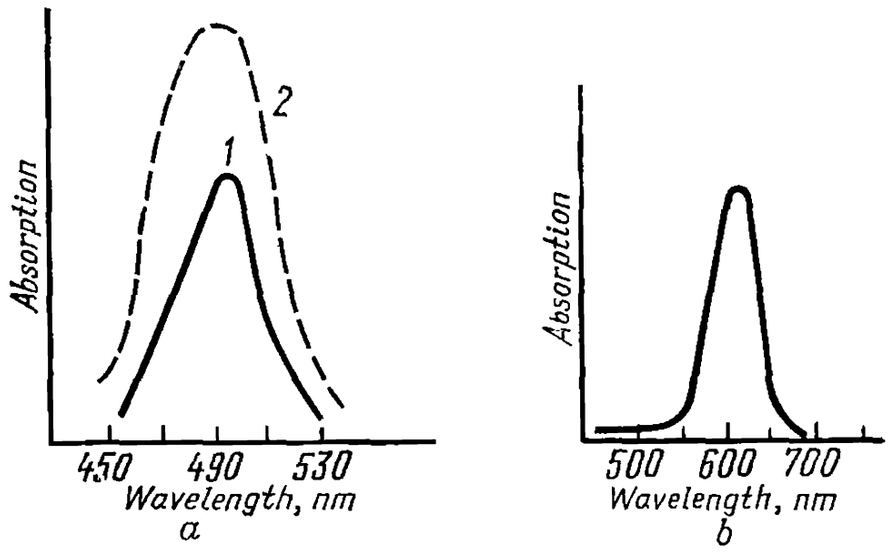


Fig. 88. Absorption spectrum:
a — $Co(OH_2)_6^{2+}$ (*1*) and $Co(NH_3)_6^{2+}$ (*2*); *b* — $Co(NCS)_4^{2-}$ in the visible region

6. (a) Determine the wavelength corresponding to the absorption maximum and predict the colour of the aquo complex of cobalt(II) (Fig. 88).

(b) What is the colour of the solutions obtained by the reaction of cobalt, its oxide and hydroxide with dilute acid? Write reaction equations.

Experiment 2. Effect of structure on the colour of Co(II) compounds. In which of the following crystal hydrates are the unit cells hexaaquo complexes of Co(II): $CoCl_2 \cdot 2H_2O$, $CoSO_4 \cdot 7H_2O$, $CoCO_3 \cdot 6H_2O$, $CoCl_2 \cdot H_2O$, $Co(NO_3)_2 \cdot 6H_2O$?

Experiment 3. Synthesis of $Co(NO_3)_2 \cdot 6H_2O$. Calculate the quantity of the starting substances to obtain the required amount of $Co(NO_3)_2 \times$ $\times 6H_2O$ by an exchange reaction between $CoCO_3 \cdot 6H_2O$ and 35-40 per cent solution of HNO_3.

Place $CoCO_3 \cdot 6H_2O$ by small portions into a porcelain dish or a beaker containing 30-40 per cent HNO_3. Filter the solution to separate surplus salt, acidify with nitric acid and evaporate on a water bath at 45-50°C until crystals begin to precipitate*. Cool

* At temperatures above 55.5°C, $Co(NO_3)_2 \cdot 6H_2O$ melts in its water of crystallization, and the trihydrate $Co(NO_3)_2 \cdot 3H_2O$ precipitates.

the solution, separate the crystals on a glass filter with suction and dry first in filter paper and then in a thermostat at 30°C.

7. The results of thermal study of the RbCl-$CoCl_2$ system are shown in Fig. 89.

(a) What compounds are formed in this system and what is the acid-base function of $CoCl_2$ in this process?

(b) Characterize the structure and stability of the anion complexes of cobalt(II).

(c) Consider the absorption spectrum (see Fig. 88*b*), determine the wavelength of the absorption maximum and predict the colour of the tetrahedral complex using $[Co(CNS)_4]^{2-}$ as an example.

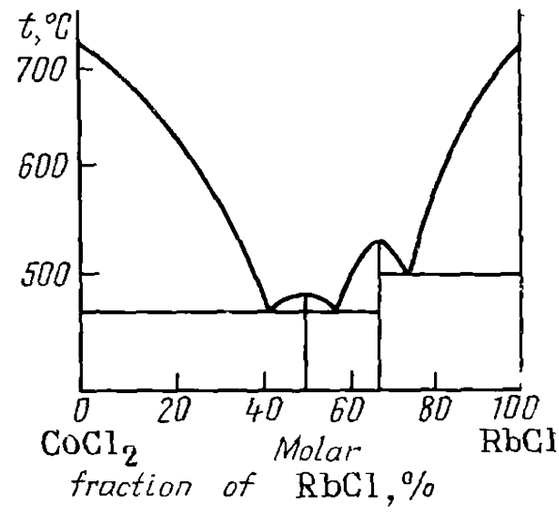


Fig. 89. Phase diagram of the system RbCl-$CoCl_2$

Experiment 4. Formation and decomposition of the thiocyanate complex of Co(II). (Qualitative test for Co^{2+} ion). Add a small amount of amyl alcohol and ether to cobaltous chloride solution and then a few drops of concentrated potassium thiocyanate solution. Mix thoroughly. Note the colour of the organic layer. Dilute with water and observe the reaction. Explain your observations.

Experiment 5. Formation and decomposition of cobalt(II) tetrachloride complex. Add concentrated hydrochloric acid to concentrated cobaltous chloride solution until the colour changes. Dilute the solution with water. Explain your observations.

Experiment 6. Dehydration of $CoCl_2 \cdot 6H_2O$. Place a few drops of concentrated cobaltous chloride solution into three test tubes. Add $CaCl_2$ crystals to the first of them and alcohol to the second one. Note the changing colour. Dilute the solutions with water. Heat the third test tube and cool. Explain your observations.

8. Heating $CoCl_2 \cdot 6H_2O$ crystals changes their colour:

$$\underset{\text{pink}}{CoCl_2 \cdot 6H_2O} \xrightarrow{49\,^\circ C} \underset{\text{pink}}{CoCl_2 \cdot 4H_2O} \xrightarrow{58\,^\circ C} \underset{\text{red-violet}}{CoCl_2 \cdot 2H_2O} \xrightarrow{140\,^\circ C} \underset{\text{blue}}{CoCl_2}$$

(a) Describe the structure of $CoCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 2H_2O$ and $CoCl_2$.

(b) Why do the melting points of $CoCl_2 \cdot 6H_2O$ (m.p. 86°C) and $CoCl_2$ (m.p. 740°C) differ greatly?

(c) How does the changing colour of the crystal hydrates of cobaltous chloride agree with their changing structure and the value Δ of the unit cells?

(d) $CoCl_2$ is used for measuring humidity by a hygrometer. Explain why.

Experiment 7. Thermal decomposition of $CoCl_2 \cdot 6H_2O$. (a) Place $CoCl_2 \cdot 6H_2O$ crystals into a dry test tube and heat carefully over a burner (hold the test tube in the horizontal position). Explain your observations.

(b) Dip a glass rod in $CoCl_2$ solution and draw a character or a figure on a sheet of paper. Warm the paper. Explain the development of sympathetic ink and vanishing of the symbols on cooling.

Experiment 8. Cobalt chloride paper and its properties. Impregnate a few wide tapes of coarse-pore filter paper in $CoCl_2 \cdot 6H_2O$ solution (5 g of the salt in 5 ml of water). Dry the paper at 100°C in a drying cabinet and keep in a desiccator.

Expose the paper to steam. Then hold it carefully over a burner. Explain your observations.

9. Explain the thermodynamic probability of oxidation of $Co(OH)_2$ to $Co(OH)_3$ by oxygen.

Experiment 9. Cobalt(II) hydroxide. Obtain cobalt(II) hydroxide by an exchange reaction. Note the change in the colour of the precipitate when excess alkali is added and the solution is heated. Study the acid-base properties of $Co(OH)_2$.

Explain what happens when the precipitated hydroxide is stirred.

10. Compare the thermodynamic probability of formation of CoS by an exchange reaction using solutions of H_2S and Na_2S.

Experiment 10. Cobaltous sulphide. (a) Test the attitude of a cobalt(II) salt solution to solutions of hydrogen sulphide and ammonium sulphide. Explain the different results of the experiments.

(b) Test the attitude of cobaltous sulphide precipitate to dilute hydrochloric acid. Explain your observations.

14.4. Compounds of Co(III), Rh(III) and Ir(III)

11. Compare the electron configuration and the magnetic properties of ammino, fluorine, cyan and ethylene diamine complexes of cobalt(III). Explain the special tendency of Co(III) to form complex compounds.

12. Give the overall stability constants of ammino complex and ethylene diamine complex of Co(III). What is the main cause of the different stabilities of the complexes?

13. Give standard oxidation-reduction potentials of the systems $Co(OH_2)_6^{3+}/Co(OH_2)_6^{2+}$, $Co(NH_3)_6^{3+}/Co(NH_3)_6^{2+}$ and $Co(CN)_6^{3-}/Co(CN)_6^{4-}$.

(a) Distribute the ligands in order of increasing stabilization of the oxidation stage +3 of cobalt.

(b) Which of the given complexes of Co(II) and Co(III) is the strongest reductant and which is the strongest oxidant?

(c) Which of the given complexes of Co(II) can be oxidized by air oxygen? Predict the outcome of the reaction between $CoCl_2$ and excess H_3N or KCN in the presence of oxygen. Write the reaction equations.

(d) How does the solution colour change in the transition of the $Co(NH_3)_6^{2+}$ complex into the $Co(NH_3)_6^{3+}$ complex (Fig. 90)? Explain your answer.

(e) Describe the colour of the $Co(en)_3^{3+}$ complex.

Experiment 11. Comparing the reducing properties of ammino and aquo complexes of cobalt(II). Dissolve ammonium chloride crystals in cobaltous chloride solution in a test tube and add excess concentrated ammonia solution. Note the solution colour. Explain what happens when the solution is shaken. (To accelerate the reaction, add activated carbon into the test tube: it acts as a catalyst.) Keep a solution containing the $[Co(OH_2)_6]^{2+}$ ion in the air. Will the colour of the solution change?

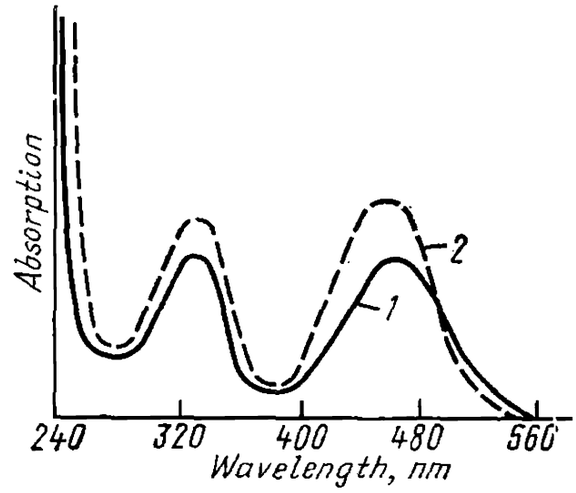


Fig. 90. Absorption spectra of $Co(NH_3)_6^{3+}$ (*1*) and $Co(en)_3^{3+}$ (*2*) in aqueous solution

14. Explain the following observations and write reaction equations. When KCN solution is added to a solution of a cobaltous compound, a red substance precipitates. When excess KCN is added, the precipitate is dissolved and the solution turns brown. When exposed to air, the solution gradually turns yellow. If the solution is shaken, it rapidly clears and turns yellow.

When a nickel(II) salt is added to the solution, a bright-green substance precipitates, while a cobalt(II) salt precipitates a pink-red substance.

Experiment 12. Obtaining cobalt(III) hydroxide. (Use the hood!) Place $CoCl_2$ solution into two test tubes and add concentrated alkali solution. Add a few drops of concentrated H_2O_2 solution into one of them and a few drops of bromine water into the other. Explain your observations. Decant the supernatant and keep the precipitates for the next experiment.

Experiment 13. Obtaining cobalt oxide Co_3O_4. (Use the hood!) Calcine the crystals $Co(NO_3)_2 \cdot 6H_2O$ obtained in Experiment 3 at 600°C in a porcelain crucible until gas stops evolving. Use the calcined product in the next experiment.

What type of oxidation-reduction obtains $CoCo_2O_4$?

Experiment 14. Oxidizing properties of oxygen compounds of Co(III). (a) Act on $Co(OH)_3$ and Co_3O_4 in two separate test tubes with dilute sulphuric acid and then add concentrated $NaNO_2$ solution. Explain your observations.

(b) Act with concentrated hydrochloric acid on $Co(OH)_3$ and Co_3O_4. Explain your observations.

15. Calcining crushed rhodium with sodium chloride in a stream of chlorine gives red crystals readily soluble in water.

(a) Explain the described process and the structure of the obtained compound.

(b) A mixture of concentrated HCl and $NaClO_3$ is the best solvent for rhodium. Explain.

16. Give examples of complex compounds which, by their composition, are intermediate between $K_3[Co(NO_2)_6]$ and $[Co(NH_3)_6]Cl_3$; between K_3RhCl_6 and $[Rh(NH_3)_6]Cl_3$.

17. Explain the following experimental data: There are red and red-violet isomers of $Co(NH_3)_5BrSO_4$. When a solution of $AgNO_3$ acts on the solution of the red-violet isomer, a white substance precipitates. From the solution of the red isomer, $AgNO_3$ precipitates a yellow substance.

18. It has been proved experimentally that the exchange of the H_2O ligand molecules of the ion $[Co(OH_2)_6]^{2+}$ for water molecules of the solution

$$[Co(OH_2)_6]^{2+} + \overset{*}{O}H_2 = [Co(OH_2)_5(\overset{*}{O}H_2)]^{2+} + H_2O$$

is 2000 times faster than a similar exchange with the ion $Co(OH_2)_6^{3+}$. Explain the different reactivity of the said complexes.

14.5. Compounds of Ir(IV)

19. What structure type are the coordination crystals of IrO_2?

20. A reaction between finely powdered iridium and sodium chloride at 300-400°C in a stream of chlorine gives a soluble derivative of Ir(IV).

(a) Explain the process.

(b) Why is the mixture of concentrated HCl and $NaClO_3$ the best solvent for iridium?

14.6. Compounds of Rh(VI) and Ir(VI)

21. Why do the hexafluorides RhF_6 (m.p. 70°C) and IrF_6 (m.p. 43.8°C, b.p. 53°C) melt and boil at low temperatures? Why do they readily sublime?

22. Characterize the oxidation-reduction properties of IrF_6 using its reaction with water, NO and Cl_2 by way of illustration.

CHAPTER 15

d-Elements of Group VIII.

The Nickel Subgroup

15.1. Elements and Simple Substances

1. Explain the character of variation of the atomic and ionic radii and the ionization energy with the atomic number of elements in the nickel subgroup.

2. Explain the character of variation of the melting points, the enthalpies of fusion and sublimation, and of the electrode potentials of the M^{2+}/M system in the series Ni-Pd-Pt.

(a) How does the chemical activity of metals in aqueous solution change in the series Ni-Pd-Pt? What curves (Fig. 85) show the variation of the corrosion rate of nickel, palladium and platinum with the pH of medium?

(b) What type of interaction is the fusion of Ni with Pd and Pd with Pt? Explain.

3. (a) What reactions occur at the electrodes during electrolysis of nickel(II) sulphate solution, if a nickel plate is used as the anode?

(b) What quantity of nickel will be deposited on the cathode if a current of 3.85 A is passed for 15 minutes?

(c) What is the industrial importance of the electrolytical manufacture of nickel?

Experiment 1. Obtaining nickel by electrolysis (nickel plating). Assemble the apparatus for electrolysis. Degrease a copper plate, etch it in hydrochloric acid, and use as a cathode. Use a nickel plate as the anode. Carry out electrolysis at room temperature, with current density of 0.3 A/dm^2 and tension across the electrode of 3.5 V. The distance between the electrodes should be 1.5 cm. Use this electrolyte for nickel plating.

15.2. Compounds of Ni(0), Pd(0) and Pt(0)

4. The composition of nickel(0) carbonyl is $Ni(CO)_4$. It is a diamagnetic compound, its dipole moment is zero. In normal conditions $Ni(CO)_4$ is liquid (m.p. —25°C, b.p. 43°C).

(a) Explain the composition and the structure of the molecule and the physical properties of $Ni(CO)_4$.

(b) What is the practical importance of nickel tetracarbonyl?

(c) Give examples of compounds of Pd(0) and Pt(0).

15.3. Compounds of Ni(II), Pd(II) and Pt(II)

5. Studies show that complexes of Pd(II) and Pt(II) are diamagnetic and most Ni(II) complexes are paramagnetic. Ni(II) complexes (unit cells) are mostly octahedral and complexes of Pd(II) and Pt(II) are plane-square.

(a) Explain these experimental facts.

(b) Describe the structure of NiO, NiF_2, $NiCl_2$ and PdO, PtO_2, $PdCl_2$, $PtCl_2$, $Pd(CN)_2$, $Pt(CN)_2$.

6. Figure 91 shows the absorption spectra of Ni(II) complexes.

(a) What is the colour of these complexes? Explain the character of the colour change in the series $[Ni(OH_2)_6]^{2+}$-$[Ni(NH_3)_6]^{2+}$-$[Ni(en)_3]^{2+}$.

(b) Write equations of reactions by which these complexes are formed.

(c) How are water molecules coordinated in the crystals of $NiF_2 \times \times 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $NiCO_3 \cdot 6H_2O$, $NiSiF_6 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$ and what is the colour of the crystals?

Experiment 2. Formation of hexaaquo complexes of nickel(II). (Use the hood!) (a) Place a piece of nickel metal in dilute nitric acid in a test tube. Explain your observations.

(b) Add dilute sulphuric acid to nickel(II) oxide and heat. Explain your observations.

(c) Compare the colour of the obtained solutions with the colour of Ni(II) crystal hydrates.

7. X-Ray structure analysis shows that the green crystals of $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ have an insular structure.

(a) The presence of what unit cells does the colour of the crystal hydrates indicate?

(b) To what ions does the compound dissociate on dissolution in water?

Experiment 3. Obtaining $(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$. Calculate the quantities of $NiSO_4 \cdot 7H_2O$ and $(NH_4)_2SO)_4$ necessary to prepare the required quantity of the wanted compound. First dissolve the substances to prepare saturated at 30°C solutions. Mix the solutions and evaporate on a water bath until crystals precipitate. Separate the precipitate on a filter, wash with a small amount of cold water and dry in blotting paper. Dissolve a portion of the precipitate in water. Compare the colour of the solution and of the crystals. Identify experimentally the ions contained in the solution.

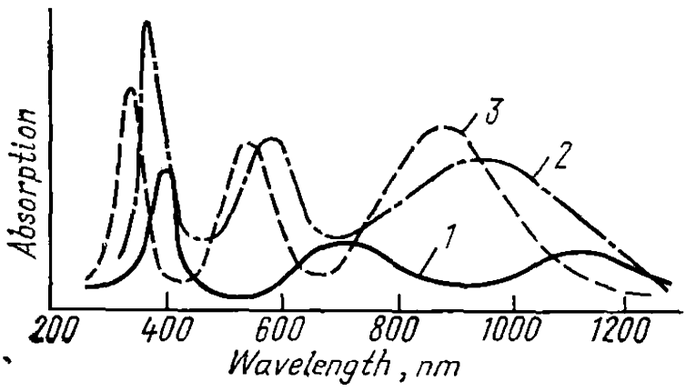


Fig. 91. Absorption spectra of the ions $Ni(OH_2)_6^{2+}$ (*1*), $Ni(NH_3)_6^{2+}$ (*2*) and $Ni(en)_3^{2+}$(*3*)

8. Determine the direction of the following reaction at 30°C:

$$Ni(OH_2)_6^{2+}(sln) + 6NH_3(sln) = Ni(NH_3)_6^{2+}(sln) + 6H_2O(l)$$

$$\Delta H^\circ_{303} = -79.5 \text{ kJ/mole}, \quad \Delta S^\circ_{303} = -92 \text{ J/deg} \cdot \text{mole}$$

(a) Write equations of the stepped process of ligand substitution. Predict the colour of the aquoammino complexes of Ni(II).

(b) How will the colour change during the reaction?

Experiment 4. Obtaining aquoammino and ammino complexes of nickel(II). Effect of ligand on colour of nickel(II) complexes. Add, by drops, concentrated ammonia solution to nickelous sulphate solution. Explain the gradual change in the colour of the solution. Keep a part of the solution for the next experiment. Test the other part with ammonium sulphide solution and acid. Explain your observations.

Experiment 5. Synthesis of $NiCl_2 \cdot 6NH_3$. (Use the hood!) Calculate the quantity of nickel dichloride necessary to obtain the required quantity of $NiCl_2 \cdot 6NH_3$. Dissolve $NiCl_2$ in the minimum water. Add concentrated aqueous solution of ammonia to dissolve the precipitate. Pass a strong current of air for 30-45 min to oxidize cobalt compounds that may be present. Filter the solution. Add a mixture of equal volumes of concentrated ammonia and ammonium chloride solution. (About 10 ml of the solution per each 4 ml of the starting $NiCl_2$ are required for complete precipitation of $NiCl_2 \cdot 6NH_3$).

Wash the precipitate 2-3 times with decantation by an ammonia solution of ammonium chloride, then with concentrated ammonia solution, alcoholic solution of ammonia and finally with alcohol.

$NiCl_2 \cdot 6NH_3$ decomposes on heating and it should therefore be dried carefully at a temperature not above 40°C and kept in a well stoppered container.

9. Variation of the Gibbs free energy in reactions of formation of the ammoniate and ethylene diamine complexes of nickel(II) at 30°C are:

$$Ni(OH_2)_6^{2+}(sln) + 6H_3N(sln) \rightleftarrows Ni(NH_3)_6^{2+}(sln) + 6H_2O(l), \quad \Delta G^\circ_{303} = -51.6 \text{ kJ/mole}$$

$$Ni(OH_2)_6^{2+}(sln) + 3en(sln) \rightleftarrows Ni(en)_3^{2+}(sln) + 6H_2O(l), \quad \Delta G^\circ_{303} = -105.2 \text{ kJ/mole}$$

(a) Prove the possibility of substitution of ethylenediamine molecules for ammonia molecules in hexaammino complex of Ni(II).

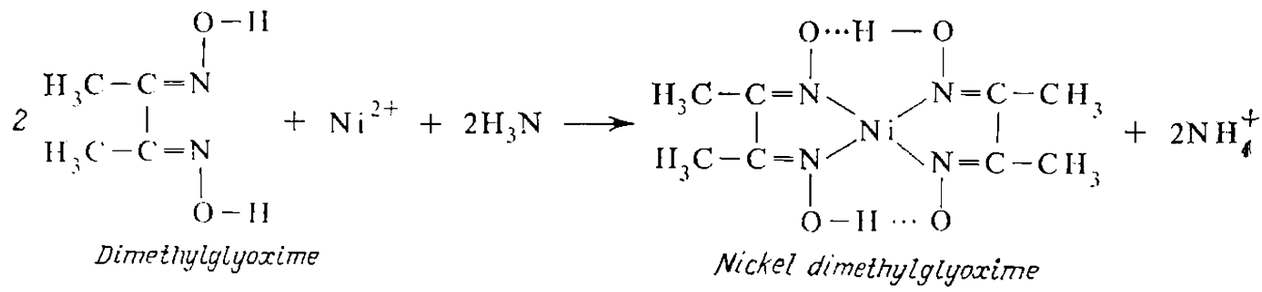
(b) Calculate the entropy variation in this reaction if the enthalpy variation $\Delta H^\circ_{303} = -25.1$ kJ/mole.

(c) Compare stability constants of the ammoniate and ethylenediamine complexes of Ni(II) and explain the difference in their stability.

(d) How does the solution change colour in this reaction (see Fig. 91)?

Experiment 6. Comparing stability of $Ni(NH_3)_6^{2+}$ and $Ni(en)_3^{2+}$. Add ethylenediamine to nickel(II) ammoniate solution. Explain your observations.

10. Chugaev's test is one of the most sensitive qualitative tests for the Ni^{2+} ion. The test is based on the formation of nickel dimethylglyoximate:



Dimethylglyoxime *Nickel dimethylglyoxime*

Characterize the dentate of the ligand in this compound. What class of complex compound is it?

Experiment 7. Obtaining nickel(II) dimethylglyoximate. Place a drop of a nickelous salt solution into a test tube. Add 3-6 drops of ammonia solution and 2-3 drops of alcoholic solution of dimethylglyoxime. Explain your observations.

11. Compare the oxidation-reduction potentials of the $E(OH)_3/E(OH)_2$ systems and ΔG°_{298} of oxidation of $E(OH)_2$ with oxygen to $E(OH)_3$ (E = Ni, Co, Fe).

(a) How does the oxidability change in the series $Ni(OH)_2$-$Co(OH)_2$-$Fe(OH)_2$?

(b) Will $Ni(OH)_2$ oxidize in open air?

Experiment 8. Nickel(II) hydroxide. Obtain nickel(II) hydroxide. Study its acid-base properties, the attitude to ammonia water and oxygen air.

Using the results of earlier experiments, compare the attitude of nickel(II), cobalt(II) and iron(II) to air.

12. Write the series of transitions from $[E(NH_3)_4]Cl_2$ to $K_2[ECl_4]$ where E is Pd(II) or Pt(II).

(a) To what ions do these compounds dissociate in solution and how does the molar electric conductivity change in this series?

(b) Which of the mentioned compounds can exist in the form of geometrical (*cis-* and *trans-*) isomers?

(c) Write reaction equations for the following experimental observations: Palladium(II) chloride, which is insoluble in water, dissolves easily in concentrated hydrochloric acid. If the obtained brown solution is acted upon by a saturated solution of potassium chloride with subsequent evaporation, a dark-yellow substance precipitates.

(d) Explain the following. When a solution on H_3N is added to a solution of $K_2[PtCl_4]$, and hydrochloric acid acts on a solution of $[Pt(NH_3)_4]Cl_2$, substances of the same composition but of different colour precipitate. In the former case, the precipitate is orange-yellow and in the latter, pale yellow.

15.4. Compounds of Pd(IV) and Pt(IV)

13. (a) What is the electron configuration of E^{4+} ions and what coordination number is characteristic of Pd(IV) and Pt(IV)?

(b) Give examples of complexes of Pd(IV) and Pt(IV). Describe their magnetic properties. To prove your answer give electronic configurations of the complexes.

14. The energy of electron transition in the ion $PtCl_6^{-2}$ is 339 and 262 kJ/mole.

(a) Calculate the absorbed wavelength and predict the colour of the ion.

(b) Crushed platinum is dissolved in aqua regia with heating. Why is the solution yellow?

15. It has been shown that electrical conductivity of millimolar solutions of some Pt(IV) compounds is as follows:

$S \cdot cm^2/mole$	$PtCl_4 \cdot 6NH_3$	$PtCl_4 \cdot 5NH_3$	$PtCl_4 \cdot 4NH_3$	$PtCl_4 \cdot 3NH_3$
	523	404	224	97

$S \cdot cm^2/mole$	$PtCl_4 \cdot 2NH_3$	$KCl \cdot PtCl_4 \cdot NH_3$	$2KCl \cdot PtCl_4$
	0	109	256

When a solution of $AgNO_3$ acts on the solutions of the last three compounds, the chloride ion is not found, while the solutions of the first four compounds precipitate AgCl which corresponds to the presence in solution of four, three, two and one mole of the Cl^- ion per mole of the compound respectively.

(a) What is the coordination structure of the given compounds?

(b) With what compounds can *cis-trans* isomerism be observed? What number of isomers can have the composition of $PtCl_4 \cdot 2NH_3$?

16. Explain the following experimental facts. A mixture of platinum black and sodium chloride is heated to 500°C in a stream of chlorine to give a yellow powder which is soluble in water. If a potassium or ammonium salt, or silver, is added to the yellow solution, yellow substances precipitate.

CHAPTER 16

d-Elements of Group I

16.1. Elements and Simple Substances

1. Construct graphs showing the variations of atomic and ionic radii, ionization energies (I_1, I_2, I_3) of the elements of the copper subgroup with their atomic number.

(a) Explain the curves.

(b) What are the oxidation states of Cu, Ag and Au?

2. (a) Explain the great difference between dissociation energies of diatomic molecules of *s*- and *d*-elements of group I.

(b) The melting, boiling and sublimation points of *d*- and *s*-elements of group I differ greatly. Explain why.

3. Give electrode potentials and compare the chemical activity of metals in the series Cu-Ag-Au in aqueous media.

4. What reactions will occur if a zinc or an iron plate is immersed into a solution of a copper(II) compound and a copper plate is immersed into a solution of a silver(I) compound?

Experiment 1. Obtaining copper and silver by chemical reduction from solution. (a) Place a saturated solution of $CuSO_4$ into a porcelain dish and add, by small portions, a precalculated quantity of zinc dust. Place the dish on a water bath and heat to 80°C. When zinc is covered with copper, decant the solution and treat the precipitate with a 5 per cent solution of hydrochloric acid. Next wash

with water (with decantation), transfer the precipitate on a filter, wash again with water and dry in blotting paper.

(b) Clean an iron plate with abrasive paper, wash it with water and immerse in a solution of cupric nitrate for 1-2 minutes. Remove the plate from the solution.

(c) Treat a copper plate with dilute nitric acid and wash with water. Apply a few drops of $AgNO_3$ solution onto the plate. Explain your observations.

5. What processes occur at the electrodes during electrolysis of cupric sulphate solution?

Experiment 2. Obtaining copper by electrolysis from solution of its compounds. (Electrolytic purification of copper.) Use the electrolyte on the basis of $CuSO_4$ in the experiment. Use an iron plate as a cathode and blister copper as an anode. Treat the copper plate with nitric acid. When the experiment is over, wash the electrodes and dry them. Keep the cathode in the air. Explain the changing appearance of the electrolytically precipitated copper.

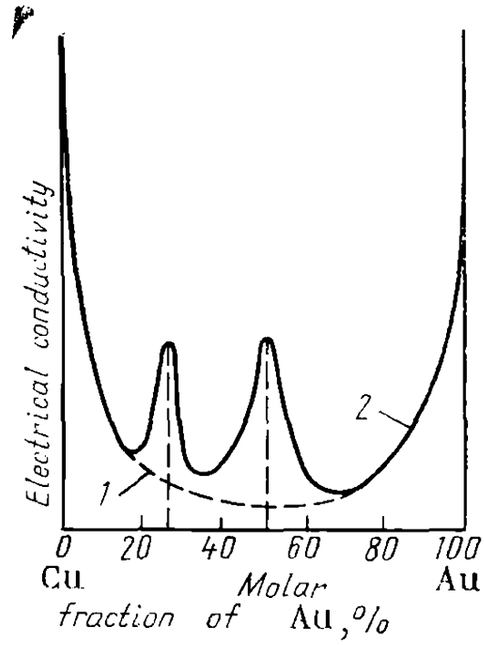


Fig. 92. Electrical conductivity of copper alloys with gold: hardened alloy (*1*), annealed alloy (*2*)

6. Make out the Born-Haber cycle to calculate the energy of the crystalline lattice of AgCl and RbCl.

(a) Why does the chemical activity of simple substances of *d*- and *s*-elements of group I differ greatly?

(b) Compare the chemical activity of copper, silver and gold with respect to chlorine and oxygen.

Experiment 3. Oxidizing copper with oxygen of air. (a) Heat a copper wire.

(b) (Use the hood!) Pour copper powder into the flame of a gas burner. Explain your observations.

Experiment 4. Oxidizing copper with sulphur. (Use the hood!) Fix a test tube containing lumps of sulphur in a stand over a dish with sand and heat carefully to melt sulphur. When the liquid boils, heat a copper foil or a thin copper wire (holding it with tongs) and put into the sulphur vapour. Explain your observations.

Experiment 5. Oxidizing copper with chlorine. (Use the hood!) Place copper foil into a glass cylinder containing chlorine. Copper gets hot and burns. Explain this fact.

7. Figure 92 shows graphically the variation of electric conductivity of copper and gold alloys with their composition. The curves describe the properties of the alloys obtained by two methods: by tempering (i.e. with rapid cooling from melting to room temperature) and by annealing (i.e. the solidified alloy is kept at a high temper-

ature for a long time and only then cooled). Figure 92 shows that the electrical conductivity of the alloy containing from 20 to 70 molar fractions of gold strongly depends on the mode of manufacture. There is only one indistinct minimum for tempered alloys and two distinct maxima for annealed alloys.

(a) Explain the great difference between the properties of tempered and annealed alloys.

(b) What compounds are formed in the system Cu-Au?

16.2. Compounds of Cu(II)

8. It has been proved experimentally that the CuL_6 octahedral complexes (unit cells) of Cu(II) are distorted tetragonally (two Cu—L bonds are longer than each of the remaining four). For example, d_{Cu-OH_2} are 0.337 and 0.259 nm in the $[Cu(OH_2)_6]^{2+}$ complex.

(a) What relationship exists between the electron configuration of the complex and its spatial structure? What electron configurations of octahedral complexes of 3*d*-elements account for regular structure and distorted structure?

(b) Write equations of stepped substitution of water molecules in Cu(II) aquo complex by ammonia molecules. Why is it difficult to introduce the fifth and the sixth ammonia molecule into the aquoammino complex?

9. Give examples of reactions by which aquo complexes of Cu(II) are formed.

Experiment 6. Formation of cupric aquo complexes. Try copper with dilute nitric acid or cuprous oxide with dilute nitric, sulphuric or hydrochloric acid. Explain the changing colour of the solution.

Experiment 7. Hydration of copper(II) sulphate. Add a few drops of water to $CuSO_4$ powder in a beaker. Explain your observations. Add water into the beaker to dissolve the salt. Use the obtained solution in Experiments 9, 10, 11.

10. Describe the coordination environment of Cu(II) in the crystals of $CuSO_4$, $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 2H_2O$.

(a) Why are these compounds of different colour?

(b) What is the colour of their aqueous solutions?

(c) As $Cu(OH_2)_6^{2+}$ converts into $[Cu(NH_3)_4(OH_2)_2]^{2+}$ and $CuCl_4^{2-}$ the colour changes to different shades. Explain why.

Experiment 8. Hydration of $CuCl_2 \cdot 2H_2O$. Dissolve $CuCl_2 \cdot 2H_2O$ crystals in water. Explain your observations.

Experiment 9. Formation of tetrachlorocuprate(II) complex and its stability. Dissolve blue vitriol in water at 90°C. Add sodium chloride crystals to the solution until the colour changes. Dilute a part of the solution with water and use the other part in Experiment 15.

Experiment 10. Formation of aquoammino complexes of copper(II). Add ammonia solution, by drops, to a strongly diluted solution of $CuSO_4$ until the precipitate dissolves. Explain your observations.

Experiment 11 Obtaining ethylene diamine complex of copper(II). Add, by drops, ethylene diamine solution to a strongly diluted solution of cupric sulphate. Compare the colour of the ammonia and ethylene diamine complexes of copper(II). Explain your observations.

Experiment 12. Properties of copper(II) hydroxide. Obtain cupric hydroxide. Examine its attitude to heat, acids, ammonia, and to concentrated alkali solution with heating. Explain your observations.

Experiment 13. Synthesis of $CuSO_4 \cdot 4NH_3 \cdot H_2O$. Calculate the mass of cupric sulphate and the volume of a 20 per cent ammonia solution (density 0.9) to obtain the required quantity of the ammoniate. (Take two calculated volumes of ammonia solution.)

Prepare a saturated at 20°C $CuSO_4$ solution (18 g of $CuSO_4$ dissolved in 100 g of H_2O at 20°C) and heat it to boiling.

Add, by small portions, ammonia solution while stirring energetically with a glass rod until the precipitate is completely dissolved.

To precipitate copper ammoniate crystals, slowly add ethyl alcohol by drops without stirring. (The volume of alcohol should be equal to the volume of the ammonia solution used in the reaction.)

Cool the solution. Separate the obtained crystals on a Büchner funnel, wash with a small quantity of alcohol or of ether and place in a dry test tube.

Prove experimentally that the obtained crystals contain the SO_4^{2-} ion and the ammoniate complex.

16.3. Compounds of Cu(I), Ag(I), Au(I)

11. How does the stability of the +1 oxidation state change in the series Cu-Ag-Au, if the energy of the electron transition $d^{10} \rightarrow d^9s^1$ is (in kJ/mole): Cu($3d^{10} \rightarrow 3d^94s^1$) 262.5; Ag($4d^{10} \rightarrow 4d^95s^1$) 469.9; Au($5d^{10} \rightarrow 5d^96s^1$) 180.5.

12. Give the overall stability constants of the ECl_2^-, EBr_2^- and EI_2^- ions.

Explain the differing stability of the halide complexes of the given complexing agent.

13. Compare the solubility products of EHal halides of the given *d*-element. Explain the different solubility of the halides.

Experiment 14. Comparing solubility of silver(I) halides. Obtain chloride, bromide and iodide of silver. Wash the precipitates with water, separate by decantation, place on a filter paper and keep in open air. Act with potassium iodide solution on a sample of silver chloride precipitate. Explain your observations.

14. Give standard oxidation-reduction potentials of the systems: Cu^{2+}/Cu^+, $Cu^{2+}/CuCl$, $Cu^{2+}/Cu(CN)_2^-$, $Cu^{2+}/CuBr$, Cu^{2+}/CuI and write equations of the corresponding half-reactions.

(a) What effect has the ligand nature on stabilization of the +1 oxidation state of copper?

(b) Will an oxidation-reduction reaction occur if solutions of KCl, KBr and KI are added to acidified solutions of Cu(II) salts?

(c) Write the equation of the reaction between solutions of $CuSO_4$ and KCN.

Experiment 15. Obtaining copper(I) chloride and chlorine complexes of copper(I). Place copper chips into a test tube containing the solution obtained in Experiment 9 and heat until the solution becomes dirty-yellow and until its few drops stop giving a blue colour when added to water. Dilute the solution with water to precipitate a white substance. Separate the precipitate by decantation and wash it with water. Keep a portion in the open air. Explain the changing colour. Treat the other part of the precipitate with hydrochloric acid (to dissolve it). Add a few drops of the obtained solution to distilled water. Explain your observations.

Experiment 16. Obtaining copper(I) iodide. Oxidizing properties of the Cu^{2+} ion. Add potassium iodide solution to a solution of a cupric compound. Add a few drops of sodium thiosulphate solution to develop the colour of the precipitate. Explain your observations.

15. Characterize the stability of the acid-base properties of EOH and E_2O.

Experiment 17. Obtaining copper(I) hydroxide and its decomposition. Add excess alkali and glucose solution to a solution of cupric sulphate. Stir the mixture thoroughly and heat. Explain the precipitation of a yellow-orange substance and its subsequent reddening on stronger heating.

Write the reaction equations assuming that glucose converts into gluconic acid:

$$CH_2OH-(CHOH)_4-C\overset{O}{\underset{H}{<}} \rightarrow CH_2OH-(CHOH)_4-C\overset{O}{\underset{OH}{<}}$$

16. Explain the following. When H_2S acts on solutions containing $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$, they precipitate a black substance. KI precipitates a yellow substance only from the former solution. If NaCl is added, precipitation is absent. How can the different stability of the complexes $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$ be explained?

17. What properties of sodium thiosulphate ("hypo") account for its use in photography?

Experiment 18. Obtaining thiosulphate complex of silver(I). Study the effect on silver halides of excess sodium thiosulphate solution. Explain your observations.

18. (a) Make your conclusions on the thermal stability of EHal and E_2O judging by ΔG_f° of their compounds.

(b) What is the practical importance of the low stability of silver compounds? Describe the essence of the photochemical decomposition of silver compounds.

Experiment 19. Photochemical decomposition of silver compounds. Expose the obtained silver compounds to light. Explain their blackening.

Experiment 20. Reduction of silver(I) compounds. Qualitative test for the Ag^+ ion. Obtaining silver mirror. Pour a solution of $AgNO_3$ into a thoroughly degreased test tube and add by drops a 2N solution of ammonia. (Shake the test tube after adding each drop.) Add ammonia until the precipitate dissolves. (Avoid adding excess H_3N.) Add an equal volume of a 10 per cent glucose solution. Stir the mixture thoroughly. Lower the test tube into a beaker containing water heated to boiling. Explain the deposition of a silver mirror on the inner surfaces of the test tube.

Pour the contents of the test tube into a special bottle for silver wastes. Dissolve the silver deposit with dilute nitric acid. Pour the solution into the silver waste bottle. Write the reaction equations.

19. Explain the following. If gold grains are dropped into a solution of sodium cyanide and air is passed into the solution, the gold dissolves. If zinc is now added to the obtained solution, gold precipitates. Why is gold readily oxidized in the presence of the CN^- ion while as strong an oxidant as HNO_3 fails to act on gold? What is the practical importance of the reaction of gold dissolution in sodium cyanide solution?

20. (a) Calculate E° of disproportionation of Cu^+ and Au^+ if the standard oxidation-reduction potentials of the systems Cu^+/Cu, Cu^{2+}/Cu^+, Au^+/Au, Au^{3+}/Au^+ are known.

(b) Characterize the comparative stability of the oxidation states of Cu and Au using the obtained data.

16.4. Compounds of Au(III)

21. Experiments show that gold(III) complexes are diamagnetic and have plane-square structure.

(a) Explain these experimental facts.

(b) Compare the structure of chlorine complexes of Au(III) and Pt(II).

(c) Describe the structure of $AuCl_3$ and $AuBr_3$.

22. What are the acid-base properties of binary gold(III) compounds? Write equations for hydrolysis of $AuCl_3$, for reactions of Au_2O_3 and $Au(OH)_3$ with acids and alkalis, and reactions between gold trihalides and halides of the alkali metals.

CHAPTER 17

d-Elements of Group II

17.1. Elements and Simple Substances

1. Analyse (preferably graphically) and explain the character of variation of the atomic and ionic radii and the three first ionization energies in the series Zn-Cd-Hg.

2. Compare the enthalpies of formation of gaseous zinc, cadmium and mercury and explain the character of variation of the melting and boiling points in the series Zn-Cd-Hg.

3. Construct a graph showing the variation of the entropy, the melting point and the melting enthalpy of simple substances of *d*-elements of 4th, 5th and 6th periods. How do the mentioned properties of the simple substances depend on the atomic structure?

4. Give the standard electrode potentials of the systems M^{2+}/M of zinc, cadmium and mercury.

(a) How does the character of E° variation in the series Zn-Cd-Hg depend on the variation of the energy effects of separate stages in the cycle:

$$\begin{array}{ccc} M(c) & \longrightarrow & M(g) \\ \downarrow & & \downarrow \\ M^{2+}(sln) & \longleftarrow & M^{2+}(g) + 2e^- \end{array}$$

(b) How does the chemical activity of metals change in the series Zn-Cd-Hg in aqueous solutions? Write equations of reactions of the metals with dilute and concentrated sulphuric and nitric acids. What effect does the metal activity have on the probability of these reactions and on the composition of the products of reduction?

Experiment 1. Comparing chemical activity of zinc and cadmium. Obtaining cadmium by reduction from solutions of its compounds. Immerse a metal zinc plate in $CdSO_4$ solution. Explain your observations. In an hour, remove unreacted zinc, separate the liberated metal on a filter, wash with hot water and dry in air.

5. How does the activity with respect to oxygen and sulphur change in the series Zn-Cd-Hg? To prove your answer, give ΔG_f° of the corresponding compounds.

Experiment 2. Obtaining sulphides by interaction of the simple substances. (Use the hood!)*

WARNING! When carrying out the experiment, NEVER bend over the mixture of sulphur and zinc. NEVER carry out the reaction in a test tube.

Mix thoroughly zinc dust and sulphur flour (2 : 1), place the mixture on an asbestos sheet, heat a glass rod over a burner and touch the mixture with it. Explain the bright flash and white fume. Grind mercury and sulphur flour in a mortar. Explain your observations.

When mercury is accidentally spilt in the laboratory, the spot where mercury might remain is treated with sulphur flour. Explain why?

6. Using values of ΔG_f° explain the following experiment.

---

* Mercury and its compounds are highly poisonous. Therefore take all precautions when handling mercury. Experiments with mercury should be performed by groups of 3-4 students under the supervision of the instructor or his assistant. All mercury wastes should be collected in a special bottle.

Experiment 3. Obtaining mercury by reduction of its compounds. (Use the hood!) Prepare a mixture of 0.5 g powdered iron with a calculated quantity of cinnabar. Place the mixture into a dry narrow test tube. Close the test tube with cotton wool and heat carefully in the flame of a gas burner.

7. What are amalgamated metals?

Experiment 4. Obtaining metal amalgams. Place a small piece of tin foil into a porcelain mortar, add a few drops of mercury and grind with a pestle into a homogeneous mass. Spilt mercury is normally gathered with a copper plate or with tin foil. Explain why.

17.2. Compounds of Zn(II), Cd(II) and Hg(II)

8. Describe the structure of ZnO and CdO crystals. What are their structure types?

9. Calculate ΔG°_{298} of reactions of zinc oxides, cadmium and mercury (II) with carbon dioxide and the H^+ ion in solution. What is the character of variation of the acid-base properties in the series ZnO-CdO-HgO?

Experiment 5. Acid-base properties of oxides. Study the attitude of ZnO, CdO and HgO to water, dilute nitric acid and concentrated alkali solution. Describe the acid-base properties of the oxides.

10. Calculate ΔG°_{298} of thermal decomposition of $Zn(NO_3)_2 \cdot 2H_2O$ and $Cd(NO_3)_2 \cdot 2H_2O$.

(a) Which of the nitrates is less stable? Explain your answer.

(b) Thermal decomposition of $Hg(NO_3)_2$ normally gives mercury rather than its oxide. Why?

(c) How are oxides of zinc, cadmium and mercury(II) obtained?

Experiment 6. Obtaining zinc oxide by oxidizing metal. Heat three zinc granules in a porcelain crucible in the flame of a burner. Keep the oxide for the next experiment.

Experiment 7. Obtaining cadmium oxide by thermal decomposition of cadmium compounds. (Use the hood!) Calcine a few crystals of $Cd(NO_3)_2$ or $CdCO_3$ in a porcelain crucible in the flame of a blow lamp until gas stops evolving.

Experiment 8. Comparing thermal stability of oxides. (Use the hood!) (a) Close a test tube containing mercury(II) oxide with glass wool and heat. Explain your observations.

(b) Heat a pinch of zinc(II) oxide on the lid of a porcelain crucible over a burner until it is red.

(c) Do the same with cadmium(II) oxide. Compare the reaction of ZnO, CdO and HgO to heating. Give explanations using values of ΔG°_f of the oxides.

11. Describe the structure and spatial configuration of aquo, ammino, hydroxy, halide and cyanide complexes of Zn(II), Cd(II) and Hg(II). Write equations for reactions by which they are obtained.

(a) How does the stability of the chlorine and iodine complexes change in the series Zn(II)-Cd(II)-Hg(II)?

(b) Will HgI_2 dissolve in excess KI solution? To prove your answer, use the values of the overall stability constant of the complex and the solubility product of HgI_2.

Experiment 9. Obtaining potassium tetraiodomercuriate. Test the reaction of mercury(II) chloride solution to deficit and excess of potassium iodide solution. Explain your observations.

Experiment 10. Obtaining ammonium tetrachlorozincate. Dissolve 70 g of anhydrous zinc chloride and 30 g of ammonium chloride in 30 ml of water with heating and then cool. Separate the precipitated crystals on a glass funnel with a porous plate.

Compare the shapes of the crystals of the obtained and original compound. Dissolve a part of the obtained crystals in water. Test for the presence of the NH_4^+, Zn^{2+} and Cl^- ions in the solution.

Compare the stability of the HgI_4^{2-} and $ZnCl_4^{2-}$ ions.

12. (a) Which of the following compounds are salts (insular lattice) and which are mixed compounds (coordination lattice): K_2HgI_4, Ag_2HgI_4, $K_2Hg(SCN)_4$, $ZnHg(SCN)_4$, $CoHg(SCN)_4$?

(b) Which of them are soluble in water?

Experiment 11. Formation of mixed thiocyanates. Using a concentrated solution of mercury (II) chloride and potassium thiocyanate solution, obtain a solution of $K_2[Hg(SCN)_4]$. Add a solution of a zinc(II) salt to a part of the obtained solution and a solution of a cobalt(II) salt to the remaining solution. Explain precipitation of a coloured substance. (If precipitation does not occur, rub the test tube wall with a glass rod.)

13. A reaction between potassium cyanide and cadmium ammoniate gives a complex cyanide. Characterize the stability of the ammino- and cyanide complexes of cadmium.

Compare the values of the overall stability constants of these complexes.

14. (a) Calculate ΔG°_{298} of the reaction between $Zn(OH)_2$ and $Cd(OH)_2$ with H^+ and OH^- ions in solution. Compare the acid-base properties of the hydroxides.

(b) Write reaction equations to illustrate the amphoteric properties of zinc amide.

(c) Write equations for reactions of zinc with aquo- and ammono acids, and with aquo- and ammono alkalis.

Experiment 12. Obtaining hydroxides of zinc and cadmium and determining their chemical nature. Obtain hydroxides of zinc(II) and cadmium(II) and determine experimentally their acid-base properties. What conditions are necessary to obtain hydroxycadmate complexes?

Experiment 13. Effect of pH on stability of hydroxyzincate complexes. Pass carbon dioxide through a sodium hydroxyzincate solution. Explain your observations.

15. Hydroxides of Zn(II), Cd(II) and Hg(II) decompose to the oxide and water at the following temperatures: $Zn(OH)_2$ at 250°C,

$Cd(OH)_2$ at 200°C, $Hg(OH)_2$ at room temperature. Explain the following experiment.

Experiment 14. Obtaining mercury(II) hydroxide and its decomposition. Study the reaction of $HgCl_2$ solution with an alkali solution. Prove experimentally the acid-base nature of the obtained precipitate.

16. What curve (Fig. 85) describes the variation of corrosion rate of zinc with pH of medium? Explain the increasing rate of metal dissolution at pH 13-14 and at pH 3-4.

Experiment 15. Reaction between zinc and alkali solution. Add sodium hydroxide solution to zinc powder and heat carefully. Explain your observations.

17. Compare E° of the systems $2Hg^{2+}/Hg_2^{2+}$, $Hg_2^{2+}/2Hg$ and Sn^{4+}/Sn^{2+}. What reaction will occur if $SnCl_2$ solution is added to $HgCl_2$ solution?

Experiment 16. Oxidizing properties of mercury(II) compounds. Add a small amount of tin(II) chloride solution to solution of $HgCl_2$ (sublimate). Explain the precipitation of a white substance and its blackening under the effect of excess $SnCl_2$ solution.

17.3. Compounds of Hg(I)

18. Force constants of the Me—Me bond in the clusters of Hg_2^{2+} and Cd_2^{2+} are 250 and 110 N/m respectively.

(a) What atomic orbitals are involved in the formation of chemical bonds in Hg_2^{2+} and Cd_2^{2+}?

(b) Which ion, Hg_2^{2+} or Cd_2^{2+}, is more stable? Explain your answer.

19. Write the equation of the Hg_2^{2+} ion disproportionation.

(a) In what direction will the reaction equilibrium shift if the sulphide, chloride, or the iodide ion is added to $Hg_2(NO_3)_2$ solution?

(b) What properties, oxidizing or reducing, are characteristic of Hg_2^{2+} compounds?

Use your answers to explain the following experiments.

Experiment 17. Disproportionation of mercury(I) compounds. (a) Add solutions of ammonium sulphide, potassium iodide and sodium chloride to mercurous nitrate solution in three separate test tubes. Explain your observations.

20. Using values of the standard electrode potentials of the systems Cu^{2+}/Cu and $Hg_2^{2+}/2Hg$ determine what reaction will occur if a copper plate is placed in a solution of a mercurous compound.

Experiment 18. Oxidizing properties of Hg_2^{2+} compounds. Clean a copper plate and apply a drop of mercurous nitrate solution onto it. Note the changes that occur on the copper surface under the drop. Wet the spot with water after 1-2 minutes, watch the affected site, and wipe it with cotton wool or filter paper. Note the colour of the precipitate.

ANSWERS AND SOLUTIONS

PART ONE

Introduction to Inorganic Chemistry

I

THE STRUCTURE OF MATTER

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Chapter 1

The Mendeleev Periodic System. The Structure of Atom

2. 6.62×10^{-19} J; 4.13 eV; 3.987×10^5 J/mol.
3. 7.36×10^6; 3.96×10^3; 6.62×10^{-21} m/s.
4. $E_1 = -1312.1$; $E_2 = -328.0$; $E_3 = -145.6$; $E_4 = -82.0$; $E_5 = -52.3$ kJ/mol.
5. 2; 1; 4.
6. 486 nm; 122 nm; 656 nm. The colour of the spectral lines can be determined from Appendix 14.
7. See Problems 4 and 6.
8. See [1], Table 11.
10. Fig. 93.
11. Fig. 94.

Chapter 2

Chemical Bonding. The Structure of Molecule

2. (a) The ground state of the molecular ion H_2^+ corresponds to the presence of the electron at the lowest energy level (σ_s) with the energy minimum at equilibrium internuclear distance. The minimum corresponds to the energy of dissociation of the molecular ion H_2^+.

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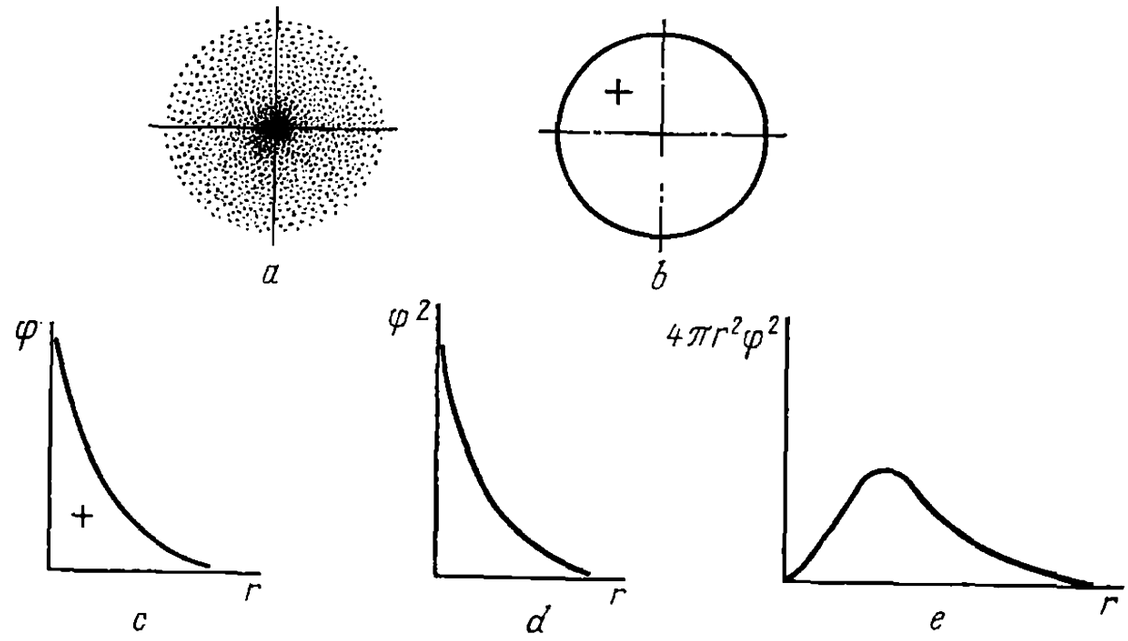


Fig. 93. Methods of describing 1*s*-state of the electron of the hydrogen atom:

a—electron cloud; *b*—interphase (with indication of the wave function sign); *c*—radial wave function; *d*—radial distribution of electron probability density; *e*—radial probability distribution of finding the electron in the atom

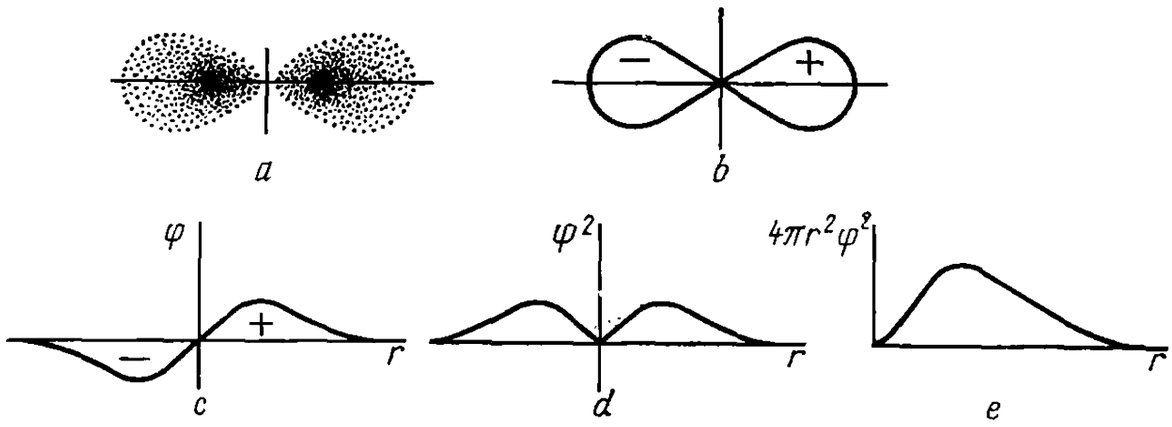


Fig. 94. Methods of describing 2*p*-state of the electron of the hydrogen atom:

a—electron cloud; *b*—interphase (with indication of the wave function sign); *c*—radial wave function; *d*—radial distribution of probability density; *e*—radial probability distribution of finding an electron in the atom

The next level (σ_s^*) has no minimum and the molecular ion H_2^+ cannot therefore be formed in this state. The orbital σ_s is therefore said to be bonding (chemical bond arises between the atoms) while the orbital σ_s^* is said to be antibonding (the chemical bond does not form).

(b) Fig. 95*a*.

(c) Fig. 95*b*.

(d) Fig. 95*c*.

(e) $(\sigma_s)^1$.

(f) When the atoms approach each other, the bond can only arise when the potential energy of the system (of the electrons and nuclei) is lowered. It becomes possible if the electrons are largely in the space between two (or more) nuclei.

3. Fig. 96.

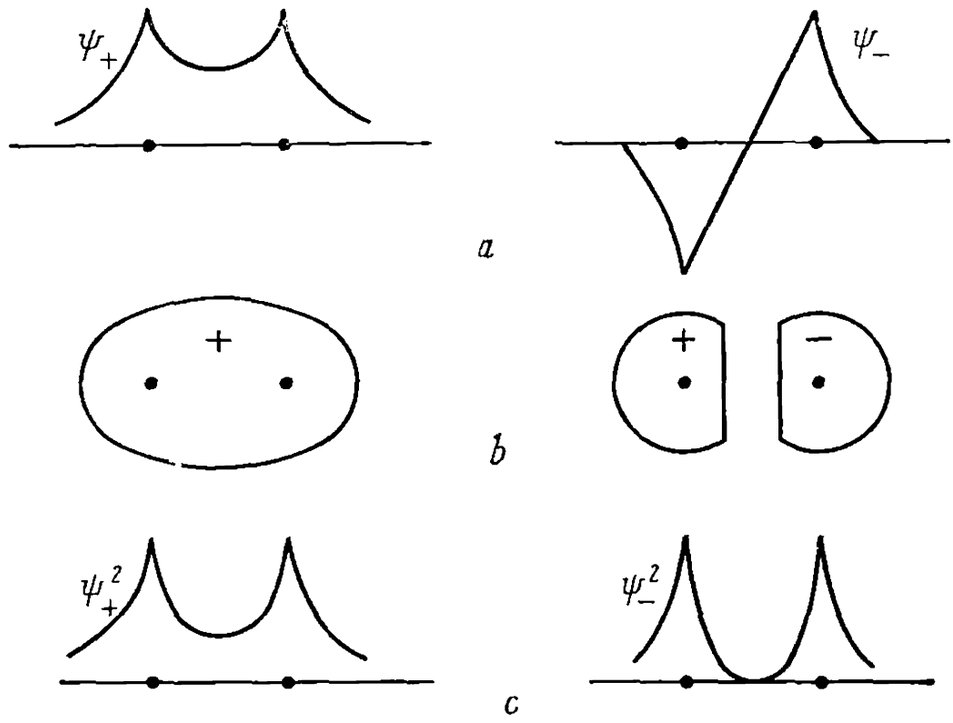


Fig. 95. Wave functions (*a*), interphase (with indication of the wave function sign) (*b*) σ_s and σ_s^*—orbitals and electron density (*c*) along the internuclear axis of the molecular hydrogen ion H_2^+

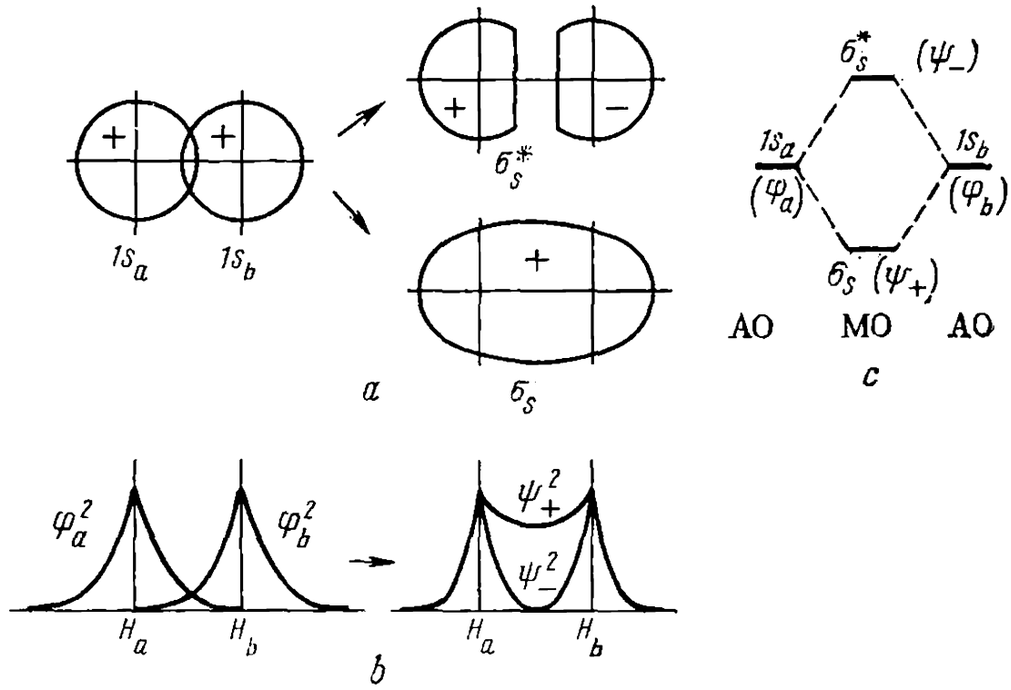


Fig. 96. Interphase boundary surfaces (*a*), curves showing the probability of finding an electron in orbitals (*b*) and energy diagram of orbitals (*c*) of the H atom and H_2^+ ion

4. (d) Strength of bond is assessed by the force constant k (N/m, force by length). The bond in the H_2 molecule is stronger since it is effected by two electrons while in the H_2^+ ion only by one electron.

6. The number and shapes of molecular orbitals of simple molecules can be determined from the number of atomic orbitals as follows:

(1) Draw the diagram of the position of the atomic nuclei of a molecule (complex) with respect to one another in the system of rectangular coordinate axes;

(2) Select the atomic orbitals which by their energy are suitable for the formation of sufficiently stable molecular orbitals. If $E_{2p} \gg E_{2s}$, the orbitals arising with the combinations of atomic orbitals $2s$-$2s$ and $2p$-$2p$ are energetically stable. The overlapping with the combination $1s$-$1s$ is insignificant and can therefore be disregarded.

(3) Select the combinations of atomic orbitals which (with respect to symmetry conditions) give molecular orbitals. Determine the type of the formed

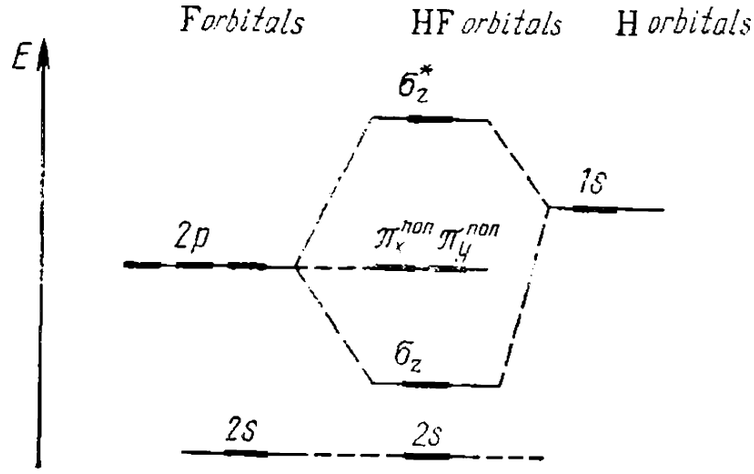


Fig. 97. Energy diagram of the orbitals of the HF molecule

molecular orbitals by the character of mutual overlapping of atomic orbitals. In our example, the combination $2s$-$2s$ gives the σ_s- and σ_s^*-molecular orbitals, the combination $2p_z$-$2p_z$ gives molecular σ_z and σ_z^*-orbitals, and the combinations $2p_x$-$2p_x$ and $2p_y$-$2p_y$ give the molecular π_x-, π_y- and π_x^*- and π_y^*-orbitals. The total number of molecular orbitals with these combinations is equal to the number of the starting atomic orbitals.

(4) Draw an approximate diagram of the energy levels (orbitals).

11. (a) The fluorine atom has $2s$ and $2p$ valency orbitals. The energy of the $1s$-orbital of hydrogen differs greatly from the energy of the $2s$-orbital of fluorine, the latter can therefore be disregarded in the formation of the bond and the $2s$-orbital of fluorine can be regarded as nonbonding orbital localized on the fluorine atom (Fig. 97).

(b) The combination of the $1s$-orbital of hydrogen and the $2p_z$-orbital of fluorine gives σ_z- and σ_z^*-orbitals. The combination of the $2p_x$- and $2p_y$-orbitals of fluorine with the $1s$-orbital of hydrogen gives zero overlapping and therefore, the $2p_x$- and $2p_y$-orbitals of fluorine in the HF molecule act as nonbonding molecular orbitals.

The electron configuration of the HF molecules is $(2s)^2\ (\sigma_z)^2\ (\pi_{x,\ y})^4$.

The bonding electrons are most of the time at the fluorine atom and the HF molecule is therefore polar.

12. According to the LCAO-MO method, the orbitals of a polyatomic molecule (complex) can be shown as a linear combination of orbitals of the central atom and group orbitals of peripheral atoms (ligands).

The beryllium atom (central atom) has the following valency orbitals: $2s$, $2p_x$, $2p_y$, $2p_z$ and the hydrogen atom has the $1s$ valency orbital. Group orbit-

als are combinations of two hydrogen atom orbitals, either with one and the same sign φ_1 or with different signs of the wave function φ_2 (Fig. 98).

In accordance with the symmetry conditions (Fig. 98), the following combinations of the central atom (beryllium) orbitals and groups orbitals (of the hydrogen atom) are possible:

$$\psi(\sigma_s) \sim \varphi_s + \varphi_1 \qquad \psi(\sigma_s^*) \sim \varphi_s - \varphi_1$$
$$\psi(\sigma_z) \sim \varphi_{p_z} + \varphi_2 \qquad \psi(\sigma_z^*) \sim \varphi_{p_z} - \varphi_2$$

There is no linear molecule for $2p_x$- and $2p_y$-orbitals of beryllium corresponding to group orbitals of the hydrogen atom with respect to symmetry. Therefore,

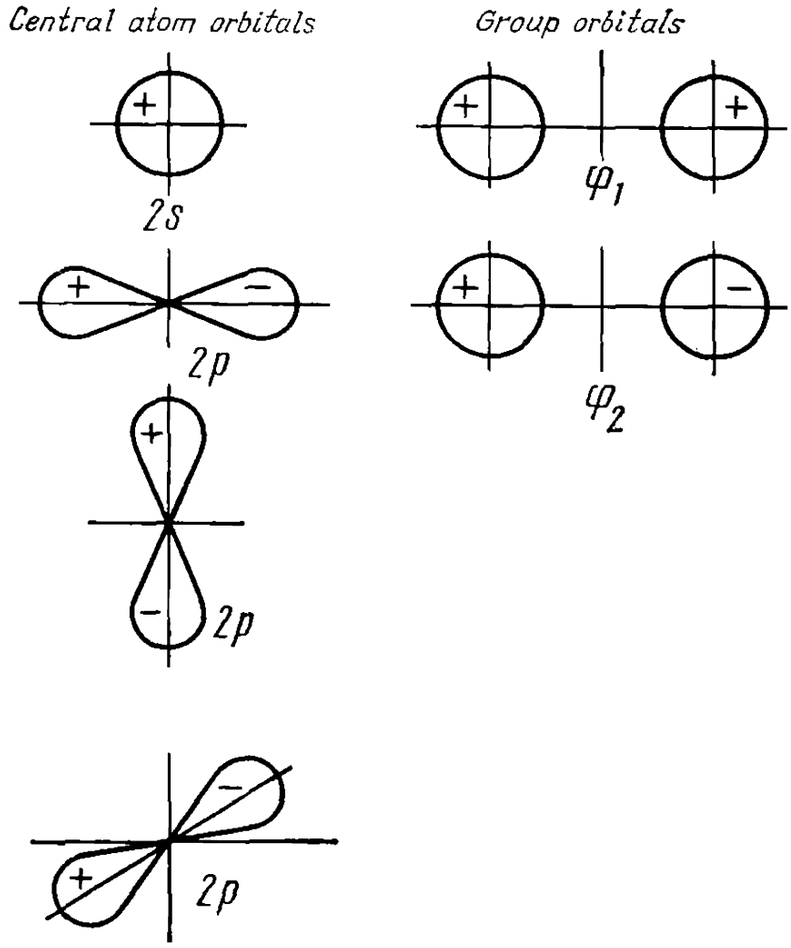


Fig. 98. Orbitals of the central atom and the corresponding (by symmetry) group orbitals of the peripheral atoms of the linear molecule

the $2p_x$- and $2p_y$-orbitals of beryllium play the role of nonbonding one-centre molecular orbitals π_x, π_y in the BeH_2 molecule.

13. See [1], Figs. 39-41.

15. (b) (See Fig. 99). Of the four valency electrons, two are on the bonding orbital and two others on nonbonding. This explains the stability of the molecule.

16. (a) At present, by valency of a chemical element is understood its ability (or a measure of its ability, in a narrower sense) to form chemical bonds.

Chemical bond can be ensured by one (H_2^+) or two electrons (H_2); it can involve two (H_2^+, H_2) or more atoms (CH_4, BeH_2, XeF_2). It indicates that the classical concept of valency, where it is expressed by the number of two-centred two-electron bonds, cannot be applied in all cases. If an atom is surrounded by n number of atoms, it does not mean that it forms n two-centre bonds.

The concept of valency is now very complicated and there is no single ap proach to the quantitative assessment of the ability of atoms to form chemica bonds. The ability of the atom to form chemical bonds with other atoms is nov generally described by three concepts: valency (covalency), oxidation state anc the coordination number of the element. There is no direct relationship betweer the numerical expression of the oxidation state, coordination number and valen cy (number of bonds).

The concept of valency as a number of two-centre and two-electron bond: can be applied to cases where the chemical bond can be regarded as localizec between two atoms of a molecule. For example, in a molecule of CH_4, the elec tron density is evenly distributed in all four hydrogen atoms and each hydroger atom is in the same condition. It car be assumed therefore that of the eigh electrons of the molecule, one electror pair is assigned to each hydrogen atom i.e. that each hydrogen atom is univa lent and is bonded with the carbon atom by a separate independent electron pair while the carbon atom is tetravalent The molecule has four equivalent bond C—H which can be represented a: follows

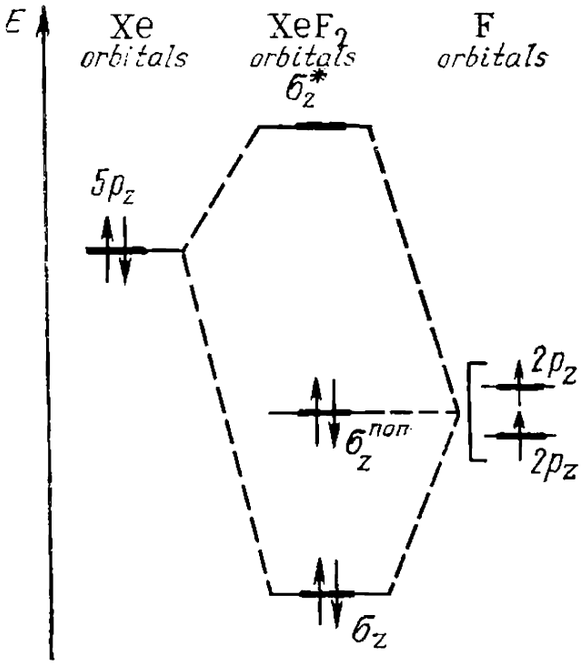
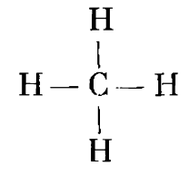


Fig. 99. The fragment of the energy diagram of orbitals of the linear three atom molecule of XeF_2



With this approach, parts are isola ted artificially from the whole molecul and the conventional character of thi approach becomes evident. But the ad vantage of this approach is its vividnes and simplicity. The concept of localize bonds are widely used to explain the spa tial configuration of molecules (com plexes).

A two-centre two-electron bond ca arise at the expense of unpaired electron of two atoms as well as at the expense of the donor-acceptor mechanism (at th expense of the electron pair of one atom and a free orbital of the other).

17. (a) The oxidation state is the formal charge on the atom if the latte consists of ions.

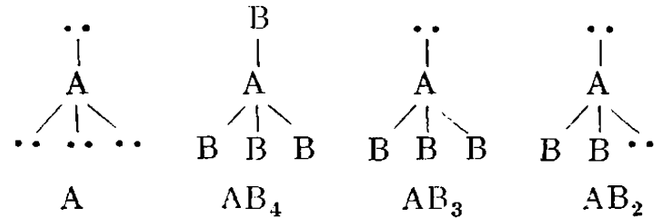
It should be noted that the oxidation state does not mean the real charg on the atoms in compounds. The oxidation state may be from —4 to +8 whil the effective charge on the atom does not exceed 2+ for positively polarize and 1— for negatively polarized atoms. The ions of the type O^{2-}, N^{3-} or C^4 have not been proved experimentally to exist in compounds as was predicte by ionic theory. For binary compounds, the ionic bond is a rarity and can cor ventionally be admitted to exist in halogen compounds with the alkali an alkaline-earth elements.

19. (a) According to the localized electron pair model, the spatial distribu tion of atoms (radicals) around the central atom of the molecule is determine by the number of its valency bonding and nonbonding (unshared) electron pair: The most probable configuration of the molecule (complex) is associated wit the maximum separation of electron pairs from one another.

(b) See Appendix 11.

(c) Owing to mutual repulsion, four σ-electron pairs of the central atom ar located at the tetrahedron vertices. Depending on the number of electron pai involved in the bond and remaining unshared, the spatial configuration corre:

ponds to the tetrahedron (AB_4), trigonal pyramid (AB_3) or angular configuration (AB_2):



(d) A bonding electron pair occupies a smaller space than a nonbonding pair. Nonbonding pairs (n.p.) are therefore more repelled from one another than bonding pairs (b.p.). Hence the repulsion effect decreases in the following order: n.p.-n.p. > n.p.-b.p. > b.p.-b.p.

Bearing this in mind, the bond angle ∠BAB decreases with an increasing number of nonbonding electron pairs in the series of the discussed molecules (AB_4-AB_3-AB_2).

20. See Appendix 11.

21. The space occupied by a bonding electron pair decreases with increasing electronegativity of peripheral atoms. This can account for the fact that molecules of the same spatial configuration have smaller bond angle in fluoride compounds than in hydrogen compounds of the same element.

22. (a) The hybridization model is based on the concept that chemical bonds are formed in the direction of the maximum overlapping of electron clouds of the interacting atoms. According to this model, the spatial configuration of the molecule is determined by the spatial arrangement of hybrid orbitals of the central atom.

(b) See Appendix 11.

23. The following operations should be performed to determine the spatial configuration of simplest molecules (complexes):

(1) Write the electron configuration and distribute the electrons in valency orbitals of the central atom (c.a.) and peripheral atoms (ligands).

(2) Determine the number of electrons involved in bonding from the oxidation state of the central atom.

(3) Determine the presence in the central atom of nonbonding electron pairs by the difference of the total number of its valency electrons and the electrons involved in bonding.

(4) Determine the number of σ-bonding electron pairs from the coordination number of the central atom.

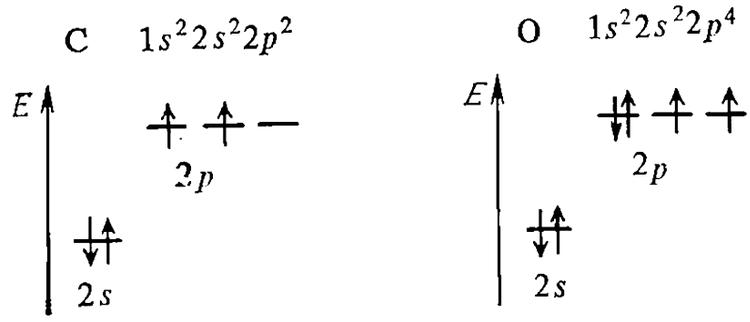
(5) Establish the spatial configuration of the molecule from the total number of bonding and nonbonding σ-electron pairs in the central atom. Determine the hybridization type of valency orbitals of the central atom which is applicable to describe the found configuration of the molecule.

(6) Determine the possibility of π-bonding.

(7) Draw the structural formula of the molecule (complex) with an indication of the delocalization of π-bonds and charges.

(8) Check if the drawn structural formula agrees with the values of bond lengths and bond angles derived from the magnetic and electrical properties of the compounds.

Consider the spatial configuration of a molecule of carbon(IV) oxide, CO_2. The carbon and oxygen atoms have the following electron configurations:



The oxidation state of carbon in CO_2 is +4. Hence all four valency electrons of the central atom are involved in the formation of bonds. The number of nonbonding electron pairs is zero.

The coordination number 2 of the central atom corresponds to two σ-bonding electron pairs, i.e. the CO_2 molecule is linear (see Appendix 11). According to the hybridization model, one *s*- and one *p*-orbital of the central atom are involved in the formation of two σ-bonds, i.e. *sp*-hybridization of valency orbitals of carbon takes place:

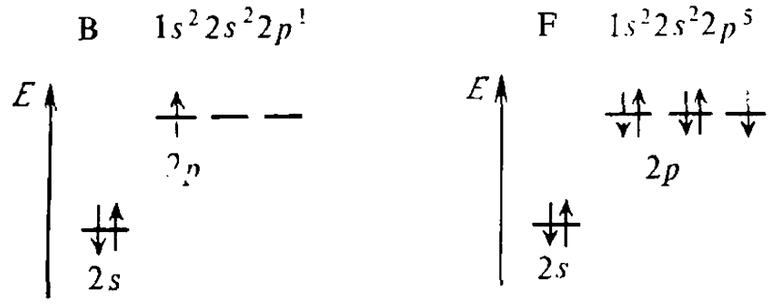
$$O \overset{\sigma}{\underset{sp}{---}} C \overset{\sigma}{\underset{sp}{---}} O$$

Two electrons of carbon which were not used in σ-bonding and one electron from each oxygen atom are involved in the formation of π-bonds. The structure of the CO_2 molecule can be expressed by the following structural formula:

$$O \overset{\sigma}{\underset{\pi}{=}} C \overset{\sigma}{\underset{\pi}{=}} O$$

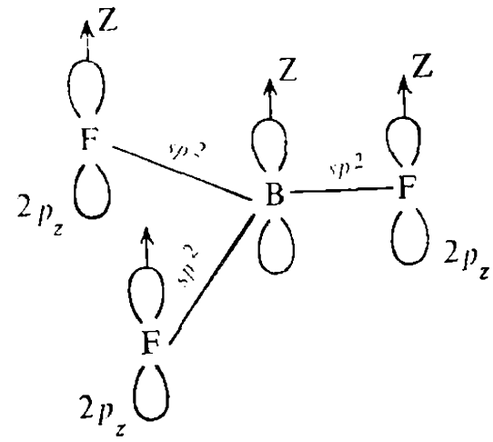
This structure well agrees with the properties inherent in the molecule of CO_2.

24. From the electron configurations of the atoms of boron and fluorine



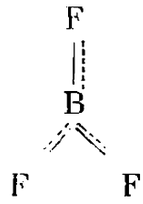
it follows that with the +3 oxidation state, all valency electrons of boron (central atom) are involved in the formation of bonds. Nonbonding electrons are absent. The molecule BF_3 (the coordination number of boron is 3) has three bonding electron pairs located around the boron atom at the vertices of a planar triangle which corresponds to the sp^2-hybridization of the boron orbitals (see Appendix 11). The BF_3 molecule is triangular.

When three σ-bonds are formed, the boron atom has one free valency 2*p*-orbital, and the fluorine atom has unused 2*p*-electron pairs:



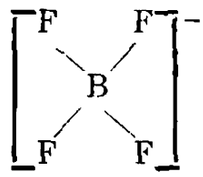
It follows that one nonlocalized π-bond can be formed between the boron atom and three fluorine atoms by the donor-acceptor mechanism. This corresponds

to 1/3 increase of the mean multiplicity of the B—F bond



and to the shortening of the internuclear distance.

In the BF_4^- ion, the boron atom has three σ-bonding electron pairs located tetrahedrically. Thus, the ion BF_4^- has the shape of a tetrahedron with the boron atom in the centre that corresponds to the sp^3-hybridization of the valency orbitals of boron



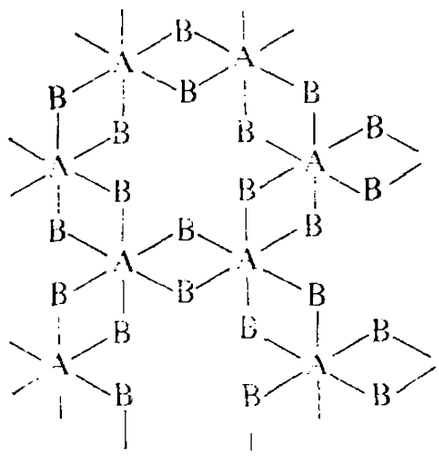
Since the boron atom has used all its valency orbitals to form σ-bonds, π-bonds are absent in the ion BF_4^-. The multiplicity of the BF bond in the BF_4^- ion is unity and the bond is therefore longer than in the triangular molecule BF_3.

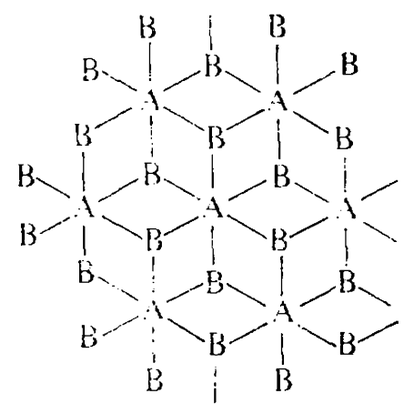
25. See Appendix 11.
26. See Appendix 11.
27. See Appendix 11.

Chapter 3

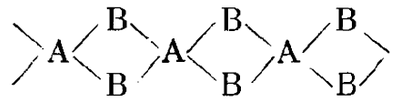
The States of Aggregation

2. 32.
3. 30.
5. Intermolecular interaction intensifies at the expense of increasing dispersion force. See, for example [1], Part One, II, Chap. 4.3.
6. The abnormal shape of the curve for hydrogen halides is explained by the appearance of the hydrogen bond between HF molecules.
8. Water molecules dissociate at the expense of the hydrogen bond.
12. (1) A_2B_7; (2) AB_3; (3) A_2B_5; (4) AB_2. See [1], Part One, III, Chap. 1.3.
13. See Problem 12.
14. (1) AB_5; (2) AB_4; (3) AB_3. See [1], Part One, III, Chap. 1.3.
15. See Problem 14.
16. (1) Rutile; (2) wurtzite and cristobalite; (3) sodium chloride; (4) corundum; (5) rhenium trioxide. See [1], Part One, III, Chap. 1.3.
17.





18. (a) See Problems 16 and 17; (b) the crystal lattice consists of the chains



(c) Unlike $BeCl_2$ and SiS_2, the crystal lattice of BeF_2 and SiO_2 is the coordination (cristobalite) type.

19. (a) Because of similarity of structure and ionic (atomic) radii.

(b) Because of the marked difference in the ionic (atomic) radii.

II

GENERAL PATTERNS AND TYPES OF CHEMICAL REACTIONS

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Chapter 4

Energy Changes in Chemical and Phase Transformations

3. −41.2 kJ/mol; −854.0 kJ/mol.
4. See Appendix 15.
8. See Appendix 15.
9. See Appendix 15.
10. (1) 1392 kJ/mol; (2) See Appendix 10.
11. If molecules contain two or more similar bonds, the breakdown energy of one of these bonds and the mean energy of these bonds are distinguished. For example, the energy of the bond CH_3—H in the CH_4 molecule, that is the heat effect of the reaction $CH_4 = CH_3 + H$, is 428.9 kJ/mol. The mean energy of the C—H bond in the CH_4 molecule is 1/4 its atomization energy, i.e. 1/4 heat effect of the reaction $CH_4 = C + H + H + H + H$, and is actually 415 kJ/mol. The mean bond energy in SiH_4 molecule is 325 kJ/mol.

The mean bond energy is calculated from the heat of atomization, i.e. the heat effect of dissociation of a given substance into free atoms. For a reaction, written in the general form as

$$AB_n = A + nB$$

the atomization heat of AB_n ($\Delta H_{at.AB_n}$) is the difference between the sum of heat of atom formation (ΔH_{fA} and ΔH_{fB}) and the heat of formation of AB_n (ΔH_{fAB_n}):

$$\Delta H_{at.\,AB_n} = (\Delta H_{f\,A} + n\Delta H_{f\,B}) - \Delta H_{f\,AB_n}$$

Once the heat of atomization is known, it is easy to calculate the mean bond energy (E_{A-B}) using this formula

$$E_{AB} = \frac{\Delta H_{at.\,AB_n}}{n}$$

12. 460.4 kJ/mol.
15. —55.6 kJ/mol H_2O.
16. —81.6 kJ/mol.
17. —94.2 kJ/mol.

Chapter 5

The Enthalpy and Entropy Factors and the Direction of a Process

2. (1) —5.0; (2) 175.7; (3) 2.9; (4) —206.3; (5) 528.9 J/deg·mol.
4. ΔH = —57.3 kJ/mol; ΔS = —72.9 J/mol·deg; ΔG = —35.6 kJ/mol. (b) Enthalpy.
5. ΔG°_{298} = 91.5 kJ/mol; ΔG^{0}_{1227} = —33.2 kJ/mol. (b) Entropy.
7. (a) At high temperature.

(c) Low temperature promotes the formation of Ag_2O and high temperature promotes its decomposition.

8. 176.2 kJ/mol; 283.6 J/mol·deg; 91.7 kJ/mol.
9. (1) —65.32; (2) —216.22; (3) —130.22; (4) —183.42 kJ/mol. The increasing negative value of ΔG in the series of reactions indicates the intensification of the basic character of the alkaline earth oxide.

Chapter 6

Chemical Equilibrium

2. $\Delta G^{0}_{298} = -RT \ln K$; $K_1 = 1 \times 10^5$.
6. $\Delta G^{\circ} = -RT \ln K_p$; $K_p = p_{CO_2}$; at p_{CO_2} = 0.1 MPa; $K_p \cong 1.4$; $\Delta G^{\circ} = 0$, then $T = \Delta H^{\circ}/\Delta S^{\circ}$.
7. (a) According to the Coulomb law, the force of electrostatic attraction F of two different charges $-q$ and $+q$ separated by the distance r is determined by the equation

$$F = \frac{q_1 q_2}{\varepsilon r^2}$$

where ε is dielectric constant; it shows how many times the force of interaction between the charges in a given medium is smaller than in vacuum.

The higher the value ε of a given solvent, the weaker the electrostatic attraction of differently charged ions. Depending on the nature of the solvent, one and the same substance can behave as a strong electrolyte (NaCl in water) and as a weak electrolyte (NaCl in benzene).

The ionization of electrolyte depends on the polarity of the solvent molecules, their ability to donor-acceptor and dative interaction with the solute and the ions, the ability of the solvent molecules to form hydrogen bonds. The energy liberated during ion solvation often compensates (or even exceeds) the energy

required to destroy the crystal lattice and to break the bonds in the solute molecules.

14. $[H^+] = 5 \times 10^{-5}$ mole/litre; $[OH^-] = 2 \times 10^{-10}$ mole/litre.

15. (1) 2; (2) 2.3; (3) 12; (4) 12.7.

17. (1) 2.56×10^{-2}; (2) 5.1×10^{-3}; (3) 6×10^{-4} mole/litre.

18. $SP = [K^{n+}]^m[A^{m-}]^n$. For a binary electrolyte ($m = n$) the solubility expressed in mole/litre is a square root of SP. The same value expressed in mole/litre is the concentration of each ion.

(a) 1.05×10^{-5} mole/litre; (b) 2.45×10^{-3} g/litre.

19. See Problem 18. AgCl 1.3×10^{-5} mole/l, 1.9×10^{-3} g/l; AgBr $2.3 \times \times 10^{-7}$ mole/l, 4.3×10^{-5} g/l; AgI 9.1×10^{-9} mole/l, 2.14×10^{-6} g/l.

Chapter 7

Reactions without Alteration of the Oxidation State of Elements

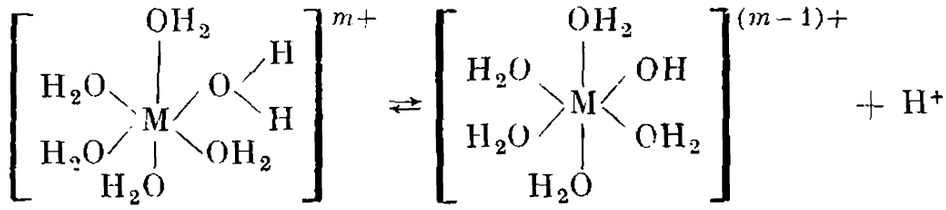
4. 1.3×10^{-4}; 5.0×10^{-14} mol/l.

7. 0.06 *N*.

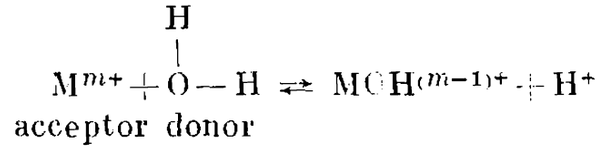
8. 167.6 ml.

10. Hydrolysis of compounds dissociating in aqueous solutions can be regarded as a result of polarization interaction of cations and anions with their hydrate shell.

Hydrolysis by cation can be represented in the form of an equation of acid ionization of the aquo complex:



Here, one H_2O molecule of the aquo complex



is polarized by the donor-acceptor interaction with the cation to convert into the OH group, while the liberated H^+ ion accounts for the acid reaction of the medium. The equilibrium

$$M^{m+}(sln) + H_2O(l) \rightleftarrows MOH^{(m-1)+}(sln) + H^+(sln)$$

is characterized by the constant

$$K = \frac{[MOH^{(m-1)+}][H^+]}{[M^{m+}][H_2O]}$$

The concentration of water changes only insignificantly during hydrolysis, and can therefore be considered constant. Thence

$$K_{hydr} = K[H_2O] = \frac{[MOH^{(m-1)+}][H^+]}{[M^{m+}]}$$

or

$$K_{hydr} = \frac{[M(OH)(OH_2)_{n-1}^{(m-1)+}][H^+]}{[M(OH_2)_n^{m+}]}$$

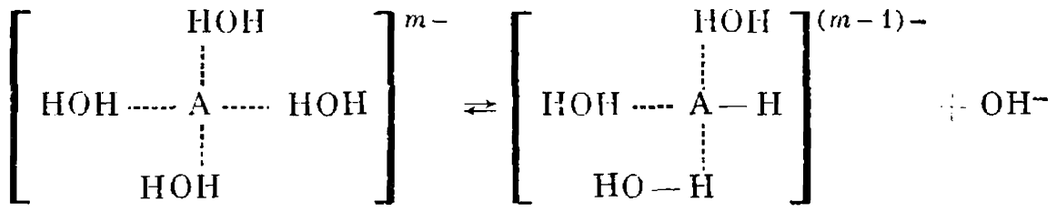
where K_{hydr} is the cation hydrolysis constant. If we assume that $[H^+] = K_w/[OH^-]$, then

$$K_{hydr} = \frac{[MOH^{(m-1)+}]\,K_w}{[M^{m+}][OH^-]} = \frac{K_w}{K_{base}}$$

Thus, hydrolysis is more intense with weaker corresponding base (with the stronger M—OH bond), i.e., with a smaller value of the constant of ionization of the base K_{base}.

It is obvious that the smaller the cation and the higher its charge, the stronger its polarizing action (the higher the accepting power) and hence the more intense hydrolysis.

11. Hydrolysis by anion can be represented as a result of the polarization interaction of an anion with the water molecules attached to it by the hydrogen bond:



$$A^{m-} + HOH \rightleftarrows A-H^{(m-1)-} + OH^-$$

donor acceptor

The hydrogen bond A...H—OH is converted into the covalent bond A—H and the OH^- ion is eliminated from the water molecule to account for the alkaline reaction of the medium.

The expression of the equilibrium constant of the reaction

$$A^{m-} + HOH \rightleftarrows HA^{(m-1)-} + OH^-$$

is

$$K = \frac{[HA^{(m-1)-}][OH^-]}{[A^{m-}][H_2O]}$$

while that for the anion hydrolysis constant is

$$K_{hydr} = K\,[H_2O] = \frac{[HA^{(m-1)-}][OH^-]}{[A^{m-}]}$$

Once it is known that

$$[OH^-] = \frac{K_w}{[H^+]}$$

we obtain

$$K_{hydr} = \frac{[HA^{(m-1)-}]\,K_w}{[A^{m-}][H^+]} = \frac{K_w}{K_{acid}}$$

Thus hydrolysis by anion is stronger with weaker acid corresponding to the anion (with stronger H—A bond), i.e. with a smaller value of the constant of acid ionization K_{acid}.

It is evident that the higher negative charge and the smaller the anion, the more readily it donates electron pairs and the easier it splits off the proton from the water molecule.

14. The overall effect of hydrolysis of a dissolved compound depends on the nature of the cations and anions found in solution. The overall hydrolysis constant (by cation and anion) is characterized by the expression

$$K_{hydr} = \frac{K_w}{K_{base}K_{acid}}$$

16. See [1], Table 23.

17. (1) 116.2 kJ/mol; (2) —124.3 kJ/mol Al^{3+} (sln).

(b) If both cation and anion interact hydrolytically with water, e.g.

$$Al^{3+} + HOH \rightleftarrows (AlOH)^{2+} + H^+$$

$$S^{2-} + HOH \rightleftarrows HS^- + OH^-$$

the ions H^+ and OH^- formed in this interaction are neutralized. It facilitates further hydrolysis precipitating an insoluble metal hydroxide and the formation of a weak acid.

18. Hydrolysis of compounds with predominantly covalent bonds differs significantly from hydrolysis of ionic and ionic-covalent compounds. Most compounds of nonmetals with nonmetals do not practically dissociate into ions in water but are irreversibly hydrolysed. The mechanism of hydrolysis of such compounds is varied and has not been sufficiently studied in many cases.

The following mechanism has been suggested to explain the hydrolysis of tetrahedral molecules of the $TiCl_4$, $SiCl_4$ and $SnCl_4$ type:

complex formation (hydration) at the expense of coordination saturation of the central atom

$$TiCl_4 + 2H_2O = [Ti(OH_2)_2Cl_4]$$

hydrolysis of the aquo complex

$$[Ti(OH_2)_2Cl_4] = [Ti(OH_2)(OH)Cl_4]^- + H^+$$

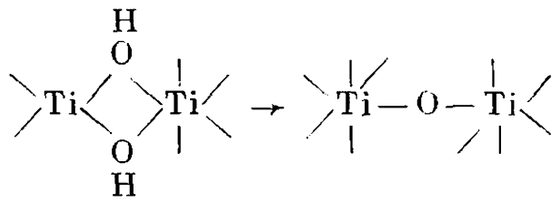
dissociation (transition of the chloride ion into solution)

$$[Ti(OH_2)(OH)Cl_4]^- = [Ti(OH_2)(OH)Cl_3] + Cl^-$$

complexation

$$[Ti(OH_2)(OH)Cl_3] + H_2O = [Ti(OH_2)_2(OH)Cl_3]$$

etc. Polymerization of the complex gives polynuclear hydroxy- and oxy-derivatives with bridge bonds of the type



Complete hydrolysis gives hydrated oxide $TiO_2 \cdot H_2O$ of variable composition.

Chapter 8

Reactions with Alteration of the Oxidation State of Elements

1. In the electron balance method, the number of gained and lost electrons is calculated by the oxidation states of the elements before and after reaction.

(1) Manganese and nitrogen change their oxidation states in this reaction:

$$\begin{array}{l|l} \overset{+7}{Mn} + 5e^- = \overset{+2}{Mn} & 2 \\ \overset{+3}{N} - 2e^- = \overset{+5}{N} & 5 \end{array}$$

The transition of Mn(VII) to Mn(II) is formally associated with the gaining of five electrons, while the transition N(III) → N(V) with the loss of two electrons. Hence $KMnO_4$ is the oxidant and $NaNO_2$ is the reductant.

The equality of the number of electrons gained by the oxidant element and the number of electrons lost by the reductant element is attained when five

moles of N(III) atoms interact with two moles of the Mn(II) atoms:

$$\overset{+7}{2Mn} + \overset{+3}{5N} = \overset{+2}{2Mn} + \overset{+5}{5N}$$

Thus, the main coefficients of the equation at the oxidant and reductant are 2 and 5. Put the found coefficients into the reaction equation

$$2KMnO_4 + 5NaNO_2 + H_2SO_4 \rightarrow 2MnSO_4 + 5NaNO_3$$

The other coefficients can be found during calculation of the balance of the other elements (minus H and O), i.e. of K and Na:

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 = 2MnSO_4 + 5NaNO_3 + K_2SO_4 + 3H_2O$$

Next the number of moles of water molecules is determined from the balance of moles of the hydrogen atoms:

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 = 2MnSO_4 + 5NaNO_3 + K_2SO_4 + 3H_2O$$

Check correctness by calculating the oxygen balance.

Since the given reaction proceeds in an aqueous solution, it can be represented as an ionic equation

$$2MnO_4^- + 5NO_2^- + 6H^+ = 2Mn^{2+} + 5NO_3^- + 3H_2O$$

(3) Auto-oxidation-reduction reaction (disproportionation)

$$\begin{array}{l|l} Cl^0 + 1e^- = Cl^{-1} & 5 \\ Cl^0 - 5e^- = Cl^{+5} & 1 \\ \hline 6Cl = 5Cl^- + Cl^{+5} & \end{array}$$

(12) In all cases where more than two elements change their oxidation state, the total number of electrons lost by the reductant and gained by the oxidant is first determined and then the procedure is as usual:

$$3As_2S_3 + 28HNO_3 + 4H_2O = 6H_3AsO_4 + 9H_2SO_4 + 28NO$$

$$\begin{array}{l|l} \left.\begin{array}{l} \overset{+3}{2As} - 4e^- = \overset{+5}{2As} \\ \overset{-2}{3S} - 24e^- = \overset{+6}{3S} \end{array}\right\} 28e^- & 3 \\ \overset{+5}{N} + 3e^- = \overset{+2}{N} & 28 \\ \hline \overset{+3}{6As} + \overset{-2}{9S} + \overset{+5}{28N} = \overset{+5}{6As} + \overset{+6}{9S} + \overset{+2}{28N} & \end{array}$$

(13) In many reactions, one of the reactants, in addition to its oxidaiton or reduction functions, performs also the function of binding the reaction products (the oxidation states of the elements are not altered). For example, when a very dilute nitric acid is reduced with magnesium powder

$$4Mg + HNO_3 + 9HNO_3 = 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$\begin{array}{l|l} \overset{0}{Mg} - 2e^- = \overset{+2}{Mg} & 4 \\ \overset{+5}{N} + 8e^- = \overset{-3}{N} & 1 \\ \hline \overset{0}{4Mg} + \overset{+5}{N} = \overset{+2}{4Mg} + \overset{-3}{N} & \end{array}$$

only one mole out of the ten used for the reaction is spent on oxidizing four moles of magnesium while the remaining nine are used to bind magnesium and ammonium ions formed in the reaction.

2. A compound, in which the element which changes the oxidation state shows its highest oxidation state, can only act as an oxidant; a compound, in which the element changing its oxidation state shows its lowest oxidation state, can act only as a reductant. If the element is found in the compound in the intermediate oxidation state, the compound can act as an oxidant in the reaction with a reductant and as a reductant in the reaction with an oxidant. This compound is capable of disproportionation.

3. The ion-electron method is used to compile equations of ionic oxidation-reduction processes. The method is based on making out special equations for reactions of reduction of the oxidant ion (molecule) and oxidation of the reductant ion (molecule) with their subsequent summation into the overall equation. The ionic equation of the reaction should first be written following the general rules for making out ionic equations, i.e. strong electrolytes should be written as ions, while weak electrolytes, gases and precipitates should be written as undissociated substances. The ions which are not changed in the course of the reaction should not be included in the ionic equation. For the reaction

$$KMnO_4 + NaNO_2 + H_2SO_4 \rightarrow MnSO_4 + NaNO_3 + K_2SO_4 + H_2O$$

the ionic equation is

$$MnO_4^- + NO_2^- + H^+ \rightarrow Mn^{2+} + NO_3^- + H_2O$$

The ion NO_2^- is oxidized to NO_3^- and the ion MnO_4^- is reduced to Mn^{2+}.

The special equation for the oxidation of the reductant ion (half-reaction) is

$$\underset{\text{reduced form}}{NO_2^-} + H_2O - 2e^- = \underset{\text{oxidized form}}{NO_3^-} + 2H^+$$

Add 1 mole of H_2O to the left part of the equation and 2 moles of H^+ to the right part (to balance the atoms in the transition from NO_2^- to NO_3^-).

To equilibrate the charges, two moles of electrons should be added to the left part of the equation.

In the special equation of the reaction, where the oxidant ion MnO_4^- is reduced to Mn^{2+}, it is necessary to add 8 moles of the H^+ ion to bind the oxygen atoms into water. Moreover, to equilibrate the charges, add 5 moles of electrons to the left part of the equation. The special equation for the reduction reaction of the oxidant ion (half-reaction) will then be

$$\underset{\text{oxidized form}}{MnO_4^-} + 8H^+ + 5e^- = \underset{\text{reduced form}}{Mn^{2+}} + 4H_2O$$

When writing the overall equation, special equations should be multiplied by coefficients so that the number of moles of the gained and lost electrons should be the same

$$\begin{array}{l|l} NO_2^- + H_2O - 2e^- = NO_3^- + 2H^+ & 5 \\ MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O & 2 \end{array}$$

The correctness of the equation can be checked by the balance of the atoms and charges in the overall equation:

$$2MnO_4^- + 5NO_2^- + 6H^+ = 2Mn^{2+} + 5NO_3^- + 3H_2O$$

The equation of the reaction in the form of formulae of non-ionized substances (if the starting substances are $KMnO_4$ and $NaNO_2$ and the medium is H_2SO_4) is

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 = 2MnSO_4 + 5NaNO_3 + K_2SO_4 + 3H_2O$$

5. $\Delta H^\circ_{298} = -38.6$ kJ/mol; $\Delta S^\circ = 637.2$ J/mol·deg; $\Delta G^\circ_{298} = -228.5$ kJ/mol $(NH_4)_2CrO_4$.

7. For the reaction written in the ionic form

	Zn^0 (c)	+ Cu^{2+} (sln)	= Cu^0 (c)	+ Zn^{2+} (sln)
ΔG_f°, in kJ/mole	0	65.56	0	−147.16

At STP, $\Delta G^\circ = -147.16 - 65.56 = -212.72$ kJ/mole

Hence, at standard temperature and pressure, the reaction direction is from left to right, i.e. zinc is oxidized while copper ion is reduced. This can be represented in the form of two oxidation-reduction half-reactions

$$Zn^0(c) - 2e^- = Zn^{2+}(sln); \qquad \Delta G^\circ = -147.16 \text{ kJ/mole}$$
$$Cu^{2+}(sln) + 2e^- = Cu^\circ(c); \qquad \Delta G^\circ = -65.56 \text{ kJ/mole}$$

Electrode (oxidation-reduction) potential E_i is used to assess quantitatively oxidation-reduction activity of substances in solution or in contact with solution:

$$-\Delta G_i = nFE_i; \qquad -\Delta G_i \text{ (J)} = 96487\ nE \text{ (V)}$$

where F is the Faraday number, n is the number of electrons involved in the elementary process.

For the reaction occurring in a voltaic cell in standard conditions:

$$-\Delta G^\circ = nFE^\circ$$

where E° is the electromotive force. As in the case of finding the value of ΔG° in the reaction, which can be calculated by the algebraic summation of the values of ΔG_f° of the reactants, the value E° can also be calculated as the difference of the standard electrode potentials E_i° of oxidation-reduction half-reactions.

Consult Appendix 22 to find the values E_i° of oxidation-reduction half-reactions:

$$Zn^0(c) - 2e^- = Zn^{2+}(sln); \qquad E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}$$
$$Cu^{2+}(sln) + 2e^- = Cu^0(c); \qquad E^\circ_{Cu^{2+}/Cu} = +0.34 \text{ V}$$

(The same values can be obtained from the equation $-\Delta G_i^\circ = nFE_i^\circ$.)

The electromotive force of the process is

$$E^\circ = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn}; \qquad E^\circ = 0.34 + 0.76 = 1.1 \text{ V}$$

Since the electromotive force can be a positive value, the process proceeds from left to right. The system Cu^{2+}/Cu, having a higher potential, performs the role of the oxidant, while the system Zn^{2+}/Zn, which is a smaller value, is a reductant.

10. According to Appendix 22, the oxidation-reduction potentials of half-reactions are

$$Sn^{4+} + 2e^- = Sn^{2+}; \qquad E^\circ = +0.151 \text{ V}$$
$$Fe^{3+} + e^- = Fe^{2+}; \qquad E^\circ = +0.771 \text{ V}$$

Their difference is a negative value (e.m.f.):

$$E^\circ = 0.151 - 0.771 = -0.620 \text{ V}$$

Hence the reaction cannot be realized. A reverse reaction, reduction of the Fe^{3+} ion with Sn^{2+} ion, is only possible:

$$2Fe^{3+} + Sn^{2+} = 2Fe^{2+} + Sn^{4+}$$

for which $E^\circ = 0.771 - 0.151 = 0.620$ V.

11. $2Fe^{3+} + 2Hal^- = 2Fe^{2+} + Hal_2$ (Hal = I, Br).

Consult Appendix 22. Electrode potentials of half-reactions are:

$$Fe^{3+} + e^- = Fe^{2+}; \qquad E^\circ = 0.771 \text{ V}$$
$$I_2 + 2e^- = 2I^-; \qquad E^\circ = 0.536 \text{ V}$$
$$Br_2 + 2e^- = 2Br^-; \qquad E^\circ = 1.065 \text{ V}$$

The electrode potential of the system Fe^{3+}/Fe^{2+} is higher than of the systen $I_2/2I^-$: $E^\circ = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{I_2/2I^-} = 0.235$ V. It indicates that the ion Fe^{3} is an oxidant with respect to the ion I^- and the reaction proceeds accordin to this equation

$$2Fe^{3+} + 2I^- = 2Fe^{2+} + I_2$$

The electrode potential of the system Fe^{3+}/Fe^{2+} is lower than that of th $Br_2/2Br^-$ system:

$$E^\circ = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Br_2/2Br^-} = -0.294 \text{ V}$$

Hence the oxidation-reduction reaction between solutions of $Fe_2(SO_4)_3$ and NaBr does not take place.

12. The electrode potential of the system $MnO_4^- + 8H^+ + 5e^- = Mn^{2+} +$ $+ 4H_2O$ is $E^\circ = 1.51$ V. It is higher than that of the system $Fe^{3+} + e^- =$ $= Fe^{2+}$, $E^\circ = 0.771$ V. Hence, the first system will act as an oxidant and the second as a reductant; the first reaction will proceed from left to right and the second from right to left. In other words, when acidified solutions of $KMnO_4$ and $FeSO_4$ are mixed together, the Fe^{2+} is oxidized to Fe^{3+} and the ion MnO_4^- is reduced to Mn^{2+}.

15. According to the Nernst equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a^x_{ox}}{\alpha^y_{red}} \quad \text{or} \quad E = E^\circ + \frac{0.059}{n} \log \frac{a^x_{ox}}{\alpha^y_{red}}$$

$$E = 0.771 + 0.059 \log \frac{0.1}{5 \times 10^{-3}} = 0.847 \text{ V}$$

16. (a) For the system

$$\underset{\text{oxidized form}}{MnO_4^-} + 8H^+ + 5e^- = \underset{\text{reduced form}}{Mn^{2+}} + 4H_2O$$

the Nernst equation is

$$E = E^\circ + \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

(activity of water $[H_2O]$ is assumed to be unity). Hence

$$(1) \quad E = 1.51 + \frac{0.059}{5} \log [1] = 1.51 \text{ V};$$

$$(2) \quad E = 1.51 + \frac{0.059}{5} \log [1 \times 10^{-2}]^8 = 1.32 \text{ V}.$$

(c) The values of pH correspond to the points of intersection of the lines in Fig. 23.

17. (b) 3.22 V.

PART TWO

Chemistry of Elements

I

s- AND p-ELEMENTS OF THE MENDELEEV PERIODIC SYSTEM

References

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Chapter 1

p-Elements of Group VII

1. The nucleus is shielded by the inner electrons, and the effective charge on the nucleus (and hence the energy of ionization of the chlorine atom) is therefore much lower than that of fluorine ($1s^2 2s^2 2p^6 3s^2 3p^5$ is the electron configuration of chlorine and $1s^2 2s^2 2p^5$ of fluorine).

Because of mutual repulsion, valency electrons of a smaller fluorine atom ($r_{orb} = 0.036$ nm) weakens the attraction to the nucleus of the additional electron ($E + e^- = E^-$) to a greater degree than the valency electrons of the larger chlorine atom ($r_{orb} = 0.072$ nm). The electron affinity of fluorine is therefore lower than that of chlorine.

The repulsion of valency electrons weakens in the series Cl-Br-I with the increasing size of the orbitals, and the main effect on the energy of ionization and electron affinity is produced by the nucleus shielded by the internal electrons.

3. (b) The lower bond energy in the fluorine molecule (as compared with the chlorine molecule) can be explained by the mutual repulsion of valency electrons in the F_2 molecule is stronger than in the Cl_2 molecule (see the answer to Problem 1). The bond energy decreases in the series Cl_2-Br_2-I_2 in accordance with the decreasing density of the overlapping bonding electron clouds.

According to another point of view, the higher bond energy in the chlorine molecule (as compared with that in the fluorine molecule) is due to π-bonding at the expense of the participation of the 3*d*-orbitals. The correctness of this explanation is now doubted.

4. See Part I, Chap. 4, Problem 8.

6. ΔH°_{298} of the reaction $P(c) + 3/2Hal_2 = PHal_3$ can be calculated from the thermochemical cycle shown in Fig. 100.

Bond energy in the fluorine molecule is weak, while the chemical bond in fluorine compounds is noted for high strength. Moreover, the activation energy for most reactions involving fluorine is insignificant.

7. (a) See Appendices 13 and 14. (b) See the answer to Problem 8.

8. The violet colour of iodine vapour is due to the electron transition from π^* to σ^* in the iodine molecule.

When iodine is dissolved in solvents whose molecules (A) show electron-donating properties, intermolecular complexes $I_2 \cdot A$ are formed at the expense

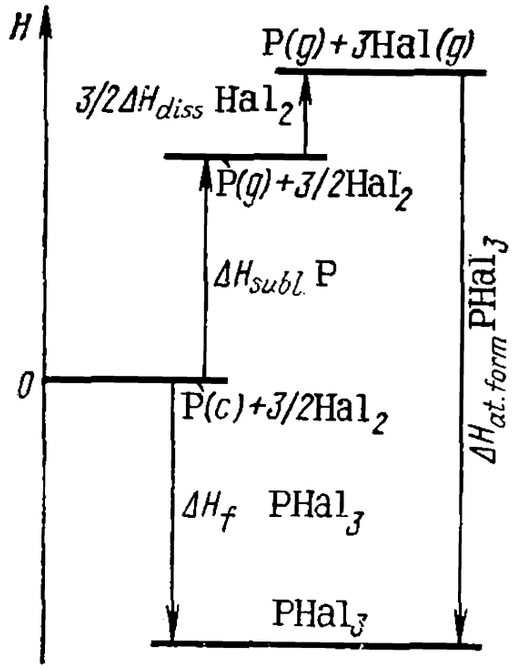


Fig. 100. Diagram for calculation of enthalpy of formation of $PHal_3$ in solution

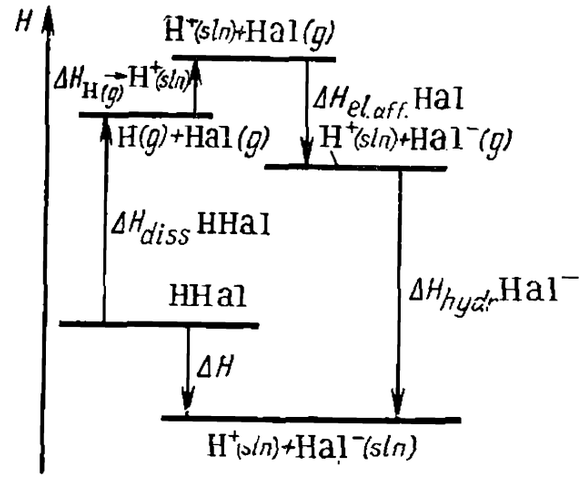


Fig. 101. Enthalpy diagram for calculation of ionization heat of HHal in solution

of the free σ^*-orbital of the iodine molecule and the electron pair of the donating molecule (n-orbital). This results in the formation of bonding and antibonding σ_c-orbital of the complex. The energy difference between π_c^*- and σ_c^*-orbitals is greater than between $\pi_{I_2}^*$ and $\sigma_{I_2}^*$-orbitals. Thus the electron transition $\pi_c^* - \sigma_c^*$ corresponds to shorter wavelength, i.e. to the displacement of the absorption band and to the change in the colour of the solution.

The coordinationally saturated molecule CCl_4 does not enter the donor-acceptor interaction with the iodine molecule and the iodine colour in carbon tetrachloride remains violet.

The value of the enthalpy of the formation of the molecular complex indicates that the interaction of iodine with the solvent is maximum in the case of triethylamine $(C_2H_5)_3N$. The absorption maximum of the iodine spectrum is shifted to shorter wavelengths and the iodine colour changes to yellow.

9. See Part One, Chap. 2, Problem 4.

10. (a) – 48.3 kJ/mol HF; —67.3 kJ/mol HCl; — 89.5 kJ/mol HBr; —103.0 kJ/mol HI.

Figure 101 shows that the acid strength increases in the series HF-HCl-HBr-HI with decreasing H—Hal bond energy. The 'abnormally' low strength of hydrofluoric acid is mainly due to the high strength of the H—F bond.

11. 12.8 kJ/mol AgF; —55.6 kJ/mol AgCl; —67.3 kJ/mol AgBr; —91.9 kJ/mol AgI; —53.1 kJ/mol CaF_2; +65.9 kJ/mol $CaCl_2$; +111.1 kJ/mol $CaBr_2$; +127.4 kJ/mol CaI_2. More negative values of ΔG correspond to lower SP.

12. 230.6 kJ/mol HF; 52.6 kJ/mol HCl; +9.0 kJ/mol HBr; —44.0 kJ/mol HI.

15. See [1], Fig. 139.

18. (a) See [I]
21. (a) See Part One, Chap. 2, Problem 15.
22. $K[SbF_6] + 2BrF_3 = K[BrF_4] + BrF_2[SbF_6]$
$K[SbF_6] + 2IF_5 = K[IF_6] + IF_4[SbF_6]$

Chapter 2

p-Elements of Group VI

1. The number of antibonding electrons increases in the series $O_2^+ [(\sigma_s)^2 (\sigma_s^*)^2 (\sigma_z)^2 (\pi_{x,\ y})^4 (\pi_{x,\ y}^*)^1]$-$O_2$ $[(\sigma_s)^2 (\sigma_s^*)^2 (\sigma_z)^2 (\pi_{x,\ y})^4 (\pi_{x,\ y}^*)^2]$-$O_2^-$ $[(\sigma_s)^2 (\sigma_s^*)^2 (\sigma_z)^2 (\pi_{x,\ y})^4 (\pi_{x,\ y}^*)^3]$. The bond order therefore decreases in the same series (2.5-2-1.5), the internuclear distance increases and the dissociation energy decreases (see Appendix 10).
2. (a) As the bond order in the series O_2-O_2^--O_2^{2-} decreases, the bond becomes less rigid which shows itself in decreasing k and $\tilde{\nu}$.

(b) The ionization energy of the oxygen molecule is lower than of the oxygen atom because during ionization of the O_2 molecule, the electron is given off from the antibonding orbital.
3. —118.1 kJ/mol $KClO_3$; 264.8 kJ/mol Na_2SO_4.
4. In the reactions under study, the negative value of ΔG_{298}° increases, which indicates the increasing acid properties in the series

$$Al_2O_3\text{-}SiO_2\text{-}P_2O_5\text{-}SO_3\text{-}Cl_2O_7.$$

5. (c) Formation of 'gas hydrates' is due to the ability of gas molecules to occupy vacant cavities in the crystal lattice of ice. Depending on the size of the molecule of the 'guest' X, the average composition of the hydrates can correspond to the formula $X \cdot 5.75\ H_2O$ (rounded to $X \cdot 6H_2O$), $X \cdot 7.75H_2O$ ($X \cdot 8H_2O$).
6. Complex formation. The displacement of the electron density of the water molecule (donor of electron pair) to the complexing agent (acceptor) decreases the electron density in the O—H bond and reduces its rigidity.The complex formation in the system $CuSO_4$-H_2O is also evidence by the liberation of heat and colour change.
7. The bond length in the ion O_2^- is 0.132-0.135 and in the ion O_2^{2-} is 0.149 nm. Hence, BaO_2 is peroxide and KO_2 is superoxide. O_2F_2 can be regarded as a covalent derivative of O_2^{2+}, $O_2[PtF_6]$ as a derivative of the ion O_2^+, and $[V(O_2)_4]^{3-}$ as a covalent derivative of O_2^{2-}.
9. (b) Because of the high positive value ΔG_f° of ozone, the formation of O_3 and O_2 is only possible in special conditions, for example, at slow electric discharge (in an ozonator) or with the absorption of ultraviolet radiation.
11. (a) See Part Two, Chap. 1, Problem 3. The ability of sulphur (oxygen, selenium) to form homo-chains is due to the presence in the atom of two unpaired electrons (two free valencies). The especially high tendency of sulphur to form polyatomic chains is explained by the high energy of the S—S bond.

(b) Ring-shaped molecules S_8 are the most stable.

(c) Rhombic and monoclinic sulphur crystals are composed of S_8 molecules. Plastic sulphur is formed by zig-zag chains.
15. Oxidation of sulphur by nitric acid can be shown in the form of half-reactions

$$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O, \quad E^\circ = 0.96\ V$$

$$SO_4^{2-} + 8H^+ + 6e^- = S + 4H_2O, \quad E^\circ = 0.36\ V$$

The first half-reaction has a higher E^0, therefore HNO_3 acts as an oxidant and S a reductant.
17. See Part One, Chap. 7, Problem 17.
18. (a) The hydrogen bond between low-polar molecules H_2S ($\mu = 1.02$ C·m) is less characteristic than that between strongly polar molecules of H_2O ($\mu = 1.84$ C·m).

19. See Part One, Chap. 7, Problem 1.

21. See Problem 11.

22. (a) Molecules are polar since there is a nonbonding electron pair at the central atom, while the molecule $SOCl_2$ has different peripheral atoms.

25. (c) The SF_6 molecule is saturated coordinationally. Hydrolysis of SF_6 does not practically occur because of the low reaction rate.

30. The dependence of the atomic radius, the ionization energy and electron affinity of *p*-elements of group VI on the atomic number of the element is similar to the variation of these constants in the series F-Cl-Br-I (see Part Two, Chap. 1, Problem 1).

31. (a) The composition of molecules becomes more complicated and the melting point increases in the series oxygen-tellurium. Polonium has a metallic lattice; it melts at a lower temperature than tellurium.

(c) See Part One, Chap. 1, Problem 3, c. $\lambda = 663.7$ nm. Electric conductivity of selenium increases in the light because the visible part of the electromagnetic spectrum ($\lambda = 663.7$ nm, red region) increases.

32. (b) See Part Two, Chap. 1, Problem 10.

34. Heat of sublimation can be calculated from ΔH_f of solid and gaseous substances

$$\Delta H_{subl} = \Delta H_{f\ EO_2(g)} - \Delta H_{f\ EO_2\ (c)}$$

Heat of sublimation increases in the series SO_2-SeO_2-TeO_2 since solid SO_2 has the molecular lattice, SeO_2 has chain and TeO_2 coordination lattice.

Chapter 3

p-Elements of Group V

1. (a) Conversion of N_2 into N_2^+ and N_2^- corresponds to the removal of the electron from the bonding orbital and to appearance of the electron in the antibonding orbital, and hence to decreased bond order, increased internuclear distance and decreased dissociation energy.

(b) During ionization of the N_2 molecule, the electron is removed from the bonding orbital. Therefore, to tear off the electron from the N_2 molecule, higher energy is required than to remove it from the N atom.

2. (a) $NaN_3(c) = Na(l) + 3/2N_2(g)$; $\Delta H^\circ_{298} = -18.8$ kJ/mole; $\Delta S^\circ_{298} = 287.2$ J/mol·deg.

$NH_4NO_2(sln)$; $\Delta H^\circ_{298} = -334.3$ kJ/mol; $\Delta S^\circ_{298} = 86.2$ /mol·deg

(b) The processes are practically irreversible, because $\Delta H < 0$, $\Delta S > 0$.

3. (a) Direct reaction between the simple substances can give only NO [$\Delta H > 0$; but $\Delta S > 0$: $\Delta S^\circ_f = S^\circ_{NO} - 1/2\ (S^\circ_{N_2} + S^\circ_{O_2})$].

For reactions of formation of other nitrogen oxides from the simple substances $\Delta H > 0$; $\Delta S < 0$ (see Part One, Chap. 2, Problem 28).

(d) High temperature, when ΔG is a negative value.

5. $\Delta S^\circ_{298} = -103.1$ J/mol·deg.

6. Valency electrons of the ammonia molecule are located in the orbitals of three energy levels, viz., two bonding and one almost nonbonding level.

8. (a) $\Delta H^\circ_{298} = 184.1$ kJ/mol; $\Delta S^\circ_{298} = 308.0$ J/mol·deg; $\Delta G^\circ_{298} = -92.3$ kJ/mol; $\Delta G^\circ_{573} = -7.6$ kJ/mol.

(2) $\Delta H^\circ_{298} = -36.1$ kJ/mol; $\Delta S^\circ_{298} = 446.4$ J/mol·deg; $\Delta G^\circ_{298} = -169.2$ kJ/mol; $\Delta G^\circ_{573} = -291.6$ kJ/mol.

(d) If an anion shows oxidizing properties (NO_3^-, NO_2^-, $Cr_2O_7^{2-}$), the decomposition of ammonium salts is irreversible (by the oxidation-reduction mechanism). If an anion has no oxidizing properties (Cl^-, PO_4^{3-}, CO_3^{2-}), the thermal dissociation into ammonia and the corresponding hydrogen compounds or the acid oxide is reversible.

9. See Part Two, Chap. 2, Problem 6.

11. Due to the higher affinity for proton, ammonia is a stronger base (donor of electron pair) and it ionizes acids to a greater degree than water.

12. (a) The second process ($\Delta G^\circ_{298} = -434.9$ kJ/mol O_2) is more probable thermodynamically than the first one ($\Delta G^\circ_{298} = -191.7$ kJ/mol O_2).

(b) Use a platinum-rhodium catalyst.

15. (a) By repulsion of nonbonding electron pairs in homochains from nitrogen atoms.

16. (c) 19438 kJ/kg N_2H_4.

(d) Hydrazine is a liquid boiling at a rather high temperature. It is unstable thermodynamically and can decompose with explosion. When it burns, much heat is liberated and the combustion products are small molecules. Hydrazine is a weak base and it decreases the danger of corrosion.

17. (a) The conversion of NO into NO^+ is associated with the loss of an electron from the π^*-orbital. The bond order is therefore higher in the NO^+ ion, its dissociation energy and the frequency of valency oscillation is higher and the internuclear distance smaller.

(b) The tendency to loosing π^*-electron is preferable.

(c) The values of $\tilde{\nu}_{NO}$ in NOCl and $NO[BF_4]$ are close to the same values in free NO molecule and in the NO^+ ion, respectively.

18. See Part One, Chap. 4, Problem 7.

21. (a) Three types of oscillations are possible in an angular molecule and one in a diatomic molecule.

23. (a) $Zn + N_2O_4 = Zn(NO_3)_2 + NO$.

(b) $NOCl + AgNO_3(c) = AgCl(c) + N_2O_4$.

(c) By dimerization of NO_2 at low temperature.

24. NO_2^+ and NO_3^-.

25. (a) By intensifying the contrapolarizing action (weakening of π-bonding in the ion NO_3^-) of the ion (atom) in the outer sphere of the compound.

(c) Thermal decomposition of $Pb(NO_3)_2$ is usually used.

27. (a) π-Electrons are delocalized more completely in the symmetrical azide ion.

(b) See Part Two, Chap. 3, Problem 25a.

28. (a) Valency electrons of the phosphorus atom are at a considerably greater distance from the nucleus ($r_{3p} = 0.092$ nm) than in nitrogen ($r_{2p} = 0.041$ nm). The energy of ionization of phosphorus is about 4 eV smaller than of nitrogen. At the same time, the mutual repulsion of electrons in one orbital in phosphorus is weaker than in nitrogen (due to larger orbitals). As a result, the electron affinity in the phosphorus atom is about 0.7 eV higher than in the nitrogen atom.

(b) The different properties of analogous compounds of phosphorus and nitrogen are explained by the different effective dimensions of the valency *s*- and *p*-orbitals of their atoms.

According to another concept, the different properties of the analogous compounds of phosphorus and nitrogen depend on the presence of vacant *d*-orbitals in phosphorus. At the present time, this latter point of view is doubted.

29. The phosphorus atoms have three unpaired $3p$-electrons, and are interconnected by pyramidal bonds. The atoms can join in a molecule P_4 or into a continuous layer $P_{2\infty}$.

30. (a) $\Delta G^\circ_{298} = 2805$ kJ/mol (1), 2233 kJ/mol (2); $\Delta G^\circ_{1773} = -78$ kJ/mol (1), -646 kJ/mol (2).

(b) Since $\Delta S > 0$, the increasing temperature facilitates the process.

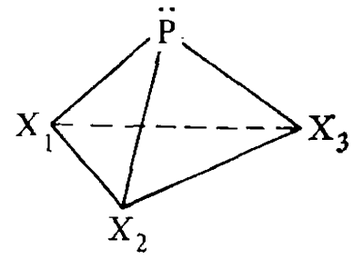
(c) The involvement of the acid SiO_2 binds the basic CaO into a stable $CaSiO_3$, decreases the endothermic character of the process, and decreases the process temperature. $p_{P_4} = 0.1$ MPa is attained at $T = \Delta H/\Delta S = 1733$ K (without SiO_2) and 1442 K (with SiO_2).

32. (b) The difference between d_{EH}, E_{EH} and μ is explained by larger orbitals and smaller EO of the P atom as compared with the atom N. The different melting and boiling points are mainly due to the different strength of the intermolecular hydrogen bond.

(c) $\Delta G^\circ_{f H_3P} > 0$. Phosphine is formed by hydrolysis of phosphides or disproportionation of phosphorus in an alkaline medium.

(d) Due to high diffusion of unshared electron pair, the electron donating power of the H_3P molecule is much lower than of the H_3N molecule. Unlike with H_3N, the ability of the H_3P molecules to act as a ligand is practically not manifested. The transition from the pyramidal molecule H_3E to the tetrahedral ion EH_4^+ is associated in the case with H_3P ($\angle HPH = 93.5°$) with a great change in the bond angle and requires higher energy than in the case with H_3N ($\angle HNH = 107.3$ °C). The stability of hydrogen compounds of phosphorus is much lower and the reducing power higher than in analogous compounds of nitrogen.

33. (a) Trigonal-pyramidal unit cell PX_3 with the electron pair at the phosphorus atom



34. (a) Electron donating power increases in the series of the trigonal-pyramidal ions ClO_3^--SO_3^{2-}-PO_3^{3-}.

(b) The reducing power increases.

35. (a) See Part One, Chap. 3, Problem 12. (d) See [1], Fig. 162.

36. (a) See Part One, Chap. 6, Problem 10.

38. See Part Two, Chap. 1, Problem 1.

39. (a) Since r_E increases and I_{ion} decreases in the series P-As-Sb-Bi, the ability to form simple substances with localized bond decreases and with delocalized bond increases. The structure changes from lamellar (nonmetal) to coordination (metal). This is confirmed by closeness of d_{EE} values in the series P-As-Sb-Bi inside and between the layers of stable modifications (see [1], Part Two, II, Chap. 4.3).

(b) It is explained by the change in the bond energy E_{EE}, which can be assessed by the different atomization energies (ΔH_f° of gaseous atoms) of simple substances. (See Appendix 15).

42. (a) The value of r_E increases along with increasing $_{EH}$, decreasing E_{EH} and stability of EH_3 molecules, which has its effect on the values of ΔH_f and ΔG_f.

(b) Affinity for proton decreases. See Problem 32.

(c) $\Delta G_f > 0$. EH_3 can be obtained by the method normally used for obtaining hydrogen compounds of nonmetals (i.e. by exchange reactions) or by reducing compounds by nascent hydrogen.

43. (b) By increasing the intermolecular interaction in the series NF_3-SbF_3 and P_2O_3-As_2O_3 and by changing the structure during the transition from SbF_3 to BiF_3 and from As_2O_3 to Sb_2O_3. Trihalides have the molecular lattice (except BiF_3 which has the coordination lattice). Crystal lattices of P_2O_3 and As_2O_3 are formed by the molecules E_4O_6; Sb_2O_3 has the lamellar lattice while Bi_2O_3, the coordination lattice.

44. −278.2; −53.5 kJ/mol ECl_3.

47. Obtained by oxidizing the simple substances or by hydrolysis of halides.

48. (a) Acidic. (b) By forming ionic compounds.

50. The potentials of the systems

$$I_2 + 2e^- = 2I^-, \quad E^\circ = 0.536 \text{ V}$$

$$H_3AsO_4 + 2H^+ + 2e^- = HAsO_2 + 2H_2O, \quad E^\circ = 0.56 \text{ V}$$

are very close to one another. The direction of the reaction depends on the pH of the medium since in accordance with

$$E = E^\circ + \frac{0.059}{n} \log \frac{[H_3AsO_4][H^+]^2}{[HAsO_2]}$$

H_3AsO_4 acts as an oxidant in an acid medium and $HAsO_2$ as a reductant. For example, at pH 8 and $[H_3AsO_4] = [HAsO_2]$ the potential of half-reaction is

$$E = E^\circ + \frac{0.059}{2} \log [1 \times 10^{-8}]^2 = 0.088 \text{ V}$$

Chapter 4

p-Elements of Group IV

4. See [I], Fig. 129.
5. See Part One, Chap. 2, Problem 14.
6. See [I], Fig. 168.
7. See Part One, Chap. 2, Problems 21 and 24.
8. See [I], Part Two, II, Chap. 5.1
9. In contrast to $COCl_2$, CF_4 and CCl_4 are coordination-saturated compounds. They are hydrolyzed, probably, through the stage at which one of the atoms is torn off. Thus, CCl_4, is hydrolyzed in the bright sunlight and practically is not hydrolyzed in the dark. The following mechanism can probably explain the process:

$$CCl_4 + h\nu = CCl_3 + Cl$$

$$CCl_3 + H_2O = \text{hydrolysis products}$$

12. See Part One, Chap. 6, Problem 6.

Na_2CO_3 2107K; $BaCO_3$ 1563K; $MnCO_3$ 622K; $PbCO_3$ 585 K

24. (a) −802.9 kJ/mol CH_4; −1426.6 kJ/mol SiH_4.
27. See Part One, Chap. 4, Problem 18.
28. (a) See Part One, Chap. 3, Problem 7.
29. See Part One, Chap. 3, Problem 12; [1]; Fig. 174
33. (a) −130.2; −92.4 kJ/mol CaO; (b) about 262° C.
37. (b) ΔH_{melt} and ΔS_{melt} are significantly higher in nonmetals with coordination lattice than in metals. Melting of nonmetals with coordination lattice is associated with the rupture of the covalent bond, increasing coordination number of the atoms and increasing internuclear distance. When germanium melts, the coordination number of its atoms increases from 4 to 8. The coordination number of carbon and silicon is also supposed to increase during their melting. When in the liquid state, carbon, silicon and germanium are metals.

Breakdown of stable bonds accounts for the sharp increase in enthalpy. The sharp change in the structure during melting is the cause of high gain in the entropy.

When metals are melted, their structure or the type of bond do not significantly change. Therefore, ΔH_{melt} and ΔS_{melt} of tin and lead are relatively low.

(c) The melting point lowers in the series C-Si-Ge-Sn, and increases in the transition from Sn to Pb. This can qualitatively be interpreted as follows. The structure of the solid phase being the same, the melting point is lower in those simple substances in the series in which the bond energy is lower. Therefore, in the series C (diamond)-Si-Ge, which have similar diamond-like structure, the melting point decreases. The structure of Sn and Pb is different. Their melting points do not obey said regularity.

The melting point depends on the equilibrium state of the solid and liquid phases. At the melting point, the Gibbs free energy is the same for the solid and for the liquid phases: $G_c = G_l$, i.e. $\Delta G = 0$ or $\Delta H_{melt} = T\Delta S_{melt}$, $T = \Delta H_{melt}/\Delta S_{melt}$.

38. (b) If the number of valency electrons in the element added is greater than in the element that forms the main crystal lattice, a semiconductor of the *n*-type is formed (excess free electrons). Conversely, if the added element has a smaller number of valency electrons (than in the main element) the *p*-type semiconductor will be formed (excess holes).

42. Strengthening of metallic character of the elements in the series Ge-Sn-Pb becomes obvious in their attitude to metals (e.g. to magnesium), to nitric and concentrated sulphuric acid.

47. (a) $Na_2[Sn(OH)_6]$.

53. 47.2 kJ/mol GeO_2; 6.1 kJ/mol SnO_2; —159.9 kJ/mol PbO_2.

Chapter 5

p-Elements of Group III

11. See Part One, Chap. 2, Problem 24.

13. (a) The different share of π-bonding in B—O.

16. (a) The formation of polymers constructed from various combinations of triangular BO_3 and tetrahedral BO_4 unit cells.

(b) See Problem 13.

24. See Part One, Chap. 3, Problem 18.

27. (a) During the interaction of $BF_3(g)$, $AlF_3(c)$, $SiF_4(g)$, $MgF_2(c)$ with KF(c), the change in the Gibbs free energy is —100.3; —30.9; —50.99 and —13.96 kJ/mol KF. This indicates decreasing acid properties of AlF_3 compared with BF_3 and also of MgF_2 compared with SiF_4.

29. (a) —126.3 kJ/mol $Ca(BO_2)_2$; —22.4 kJ/mol $Ca(AlO_2)_2$.

32. The properties of Ga, In and Tl (in contrast to B and Al) depend also on *d*-compression (*np*- and *ns*-electrons penetrate the shield of the inner $(n-1)\,d^{10}$-electrons). The properties of Tl also depend on the *f*-compression (6*p*- and 6*s*-electrons penetrate the shield of $4f^{14}$-electrons).

34. GaF_3 and InF_3 have the coordination, $InCl_3$ has the lamellar and $GaCl_3$ has the molecular lattices.

37. —32 kJ/mol $InCl_3$; —264.2 kJ/mol $TlCl_3$.

39. The compounds have diamond-like structure. (See [1], Table 43, Fig. 195.)

Chapter 6

s-Elements of Group II

4. ΔG°_{298}: +6.2 kJ/mol CaO, —59.5 kJ/mol BaO; $\Delta S^\circ_{298} = -99.1$ J/deg·mol CaO; —102.1 J/deg·mol BaO.

5. (a) $BaCO_3$ 1563 K, $Ba(NO_3)_2$ 1137 K.

6. (b) See Part I, Chap. 6, Problem 6.

7. The structure is changed. $BeF_2(g)$ has the linear structure and $BeF_2(c)$ is the coordination polymer.

8. See Part One, Chap. 3, Problem 18c.

Chapter 7

s-Elements of Group I

2. If the structure of the solid phase is similar, the melting point of the simple substances of the given subgroup depends on the energy of the bond between the entities of the solid phase, viz., between atoms in metals and between molecules (atoms) in nonmetals. The values of enthalpy of formation of simple substances in the gaseous state can be used as the measure of bond energy. The melting point lowers with growing atomic number of the metals with similar structure in the main subgroups, because the bond energy decreases with increasing radius of the atom.

The boiling point of simple substances depends on the bond energy in about the same way as in the case with the melting point.

3. All alkali metals have volume-centred cubic lattices. The difference in the phase diagrams depends mainly on the different atomic radii.

6. As the I_{ion} changes, one might expect cesium to occupy the extreme left position and lithium the extreme right position in the electrochemical series of alkali metals. Experiments show the high $E°$ value of lithium which is due to the high energy of hydration of the Li^+ ion.

10. See Part Two, Chap. 5, Problem 26.

17. (a) See Appendix 14.

II

d-ELEMENTS OF THE MENDELEEV PERIODIC SYSTEM

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Chapter 8

General Properties of the d-Elements

2. (a) There exists a reverse dependence of the ionization potential on the dimensions of the atom. Both characteristics are the result of insufficient shielding of the nucleus with *d*-electrons. This effect becomes even more appreciable with growing number of *d*-electrons. Filling of 3*d*-orbitals with one electron is completed in $Mn(3d^54s^2)$. This manifests in a certain increase in the bond energy of 4*s* electrons penetrating the shield of $3d^5$-configuration with the nucleus. The highest I_1 is in Zn $(3d^{10}4s^2)$ which agrees with complete filling of 3*d*-orbitals and with strengthened bond of 4*s*-electrons penetrating the shield of $3d^{10}$-configuration with the nucleus (see [1], Fig. 12).

17. See [1], Fig. 211.

18. See [1], Fig. 211.

20. (b) See Appendices 13 and 14.

21. A complicated theory is required in most cases to explain the absorption spectra and the colour of complexes. At the same time, with qualitative approach one can assume that the difference in the colour of the complexes formed by a given complexing agent depends on the value of Δ. The absorption shifts towards shorter wavelengths with increasing Δ and toward longer wavelengths with decreasing Δ.

In the crystals $CuSO_4 \cdot 5H_2O$ and in the aqueous solution of the sulphate, the ion Cu^{2+} is found in the field of the water molecules and is light blue. In an

ammonia solution, the colour of the sulphate changes to intense blue, which is due to the change of the ligand (ammonia instead of water). Since ammonia molecules provide for a stronger field, the absorption shifts toward shorter wavelengths. On the other hand, anhydrous $CuSO_4$ is colourless because the field of the sulphate ion is very weak and the substance absorbs in the infra-red region of the spectrum.

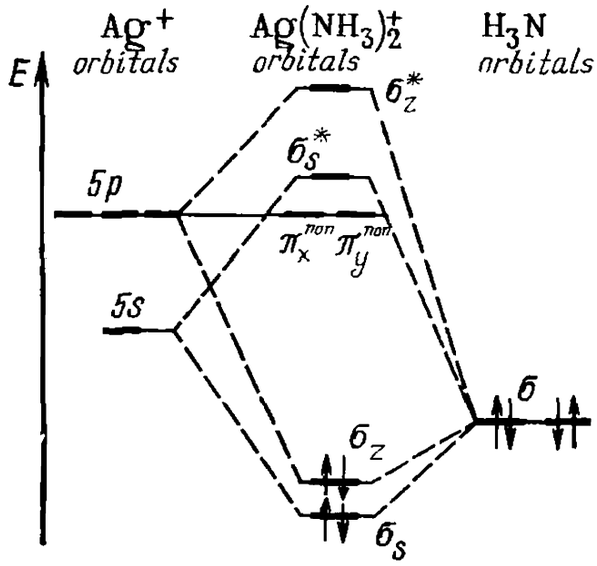


Fig. 102. Energy diagrams of orbitals of the linear complex $[Ag(NH_3)_2]^+$

22. See [1], Part Two, III, Chap. 1.4

23. (c) The complex $[Co(NH_3)_6]^{3+}$ has the electron configuration $(\sigma_s)^2(\sigma_p)^6(\sigma_d)^4(\pi_d^{non})^6$. According to the VB theory, the bonding configuration $(\sigma_s)^2(\sigma_p)^6(\sigma_d)^4$ corresponds to the involvement of six vacant d^2sp^3-hybrid orbitals of the Co^{3+} ion (acceptor) in formation of bonds with the acceptance of the electron pairs of six ligands (donor). Nonbonding configuration $(\pi_d^{non})^6$ corresponds to six electrons of the ion Co^{3+} (d^6) which is not involved in the formation of bond (see [1], Fig. 215).

By the CF theory, the nonbonding configuration $(\pi_d^{non})^6$ corresponds to filling of d_ε-orbitals of the Co^{3+} ion (d^6) in the strong field of octahedral symmetry.

24. See Part One, Chap. 2, Problem 12. Valency orbitals of the Ag^+ ion are $5s$, $5p_x$, $5p_y$ and $5p_z$. The valency orbital of ammonia is its nonbonding orbital. Group orbitals are combinations of two ligand orbitals (see Fig. 98): either with the same sign (φ_1) or with different signs of the wave function (φ_2).

It is easy to show that by the symmetry conditions (Fig. 98) the following combinations of Ag^+ orbitals and group orbitals of the ligands are possible:

$$\psi(\sigma_s) \sim \varphi_{5s} + \varphi_1 \quad \text{and} \quad \psi(\sigma_s^*) \sim \varphi_{5s} - \varphi_1;$$

$$\psi(\sigma_z) \sim \varphi_{5p_z} + \varphi_2 \quad \text{and} \quad \psi(\sigma_z^*) \sim \varphi_{5p_z} - \varphi_2$$

There are no suitable (with respect to symmetry) group orbitals of the ligands for p_x- and p_y-orbitals of silver in the linear complex. Therefore, they perform the role of nonbonding one-centre orbitals π_x and π_y.

Figure 102 shows energy levels of the complex $[Ag(NH_3)_2]^+$. Four electrons (two electrons from each ligand) fill two bonding molecular orbitals.

The electron configuration of the complex is $[\sigma_s]^2[\sigma_z]^2$ which, in accordance with the VB theory, corresponds to the involvement of the sp-hybrid orbitals of the Ag^+ ion in the formation of the donor-acceptor bond.

27. (b) See Appendix 19 and Problem 26.

28. According to Appendix 19, $K_{st} = 1.07 \times 10^{12}$, $\log K_{st} = 12.03$.

$$\Delta G^\circ = -RT \ln K_{st} = -2.303\, RT \log K_{st}$$

$$\Delta G^\circ_{298} = -2.303 \times 8.314 \times 298 \times 12.03 = -68.6 \text{ kJ/mol}$$

Chapter 9

d-Elements of Group IV

2. (a) In contrast to subgroups of s- and p-elements, the bond energy of simple substances in subgroups of d-elements increases with the atomic number. This is probably due to the increased proportion of the covalent bond formed at the expense of $(n-1)d$-orbitals.

The increasing enthalpy of formation of simple substances in the gaseous state indicates strengthening of the chemical bond. For example, for the elements of the titanium subgroup:

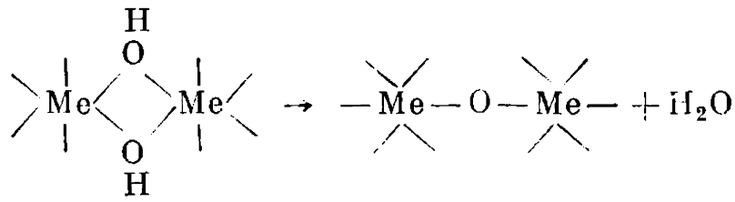
	Ti	Zr	Hf
ΔH_f°, kJ/mol	471.4	611	617.1

If the structure of the metals is similar, the melting and boiling points, the enthalpy of melting, boiling and sublimation increase with strengthening chemical bond in the series of metals (e.g. Ti-Zr-Hf). Insignificant deviations from the rule are observed with Pd in the nickel subgroup and gold in the copper subgroup. The regularities in the zinc subgroup are the same as in the subgroups of *s*- and *p*-elements.

7. —12.6 kJ/mol TiO_2 and —71.3 kJ/mol $CaTiO_3$.

(a) In the series $Ti(OH)_4$-$TiO(OH)_2$-TiO_2, the number of active ol groups Ti-OH-Ti decreases and less reactive oxol groups Ti-O-Ti appear. The structure changes from lamellar in $Ti(OH)_4$ to coordination in TiO_2. The chemical activity decreases.

(b) Decreases due to the transition of the ol groups to oxol groups:



10. —411.9 kJ/mol; —118.8 J/mol·deg.

14. See Part One, Chap. 7, Problem 18.

15. (a) Corrosion resistance of metals to H_2O, H_2SO_4(sln), HCl(sln) is due to the presence of a thin protective oxide film (EO_2) on the metal surface. When fluorides are added, hydrofluoric acid is formed which dissolves the oxide film with formation of stable fluorine complexes EF_6^{2-}. As a result, the metal rapidly reacts with any dilute acid.

(b) The oxide film (EO_2) is dissolved in HF. The role of the complexing agent in the reaction is performed by HF, while the ion OH_3^+ acts as an oxidant in hydrofluoric acid and the ion NO_3^- act as an oxidant in a mixture of hydrofluoric and nitric acid. The fluorides EF_6^{2-} and TiF_6^{3-} are formed in the reaction. (The latter fluoride is formed if hydrofluoric acid acts on titanium.)

16. —71.5 and —211 kJ/mol Zr.

(b) The carbon thermal method is not used because carbides formed contaminate the main product.

17. (a) See Appendix 14.

18. (a) TiF_3 and Ti_2O_3 have the coordination structure of the ReO_3 and Al_2O_3 type respectively, while $TiCl_3$ has the lamellar lattice of the $AlCl_3$ type.

19. (c) See Appendix 14.

21. Octahedral complexes and unit cells of these compounds have similar electron configurations. Since the values of Δ are about the same, the colour of the complexes (unit cells) is similar as well.

25. (b) $T = \Delta H/\Delta S$; at $p_{TiCl_4} = 101.325$ kPa. $TiCl_3$(c) decomposes at about 530 °C, and $TiCl_2$(c) at about 1300 °C.

Chapter 10

d-Elements of Group V

2. See Part Two, Chap. 9, Problem 2.

3. (b) It happens because carbides of vanadium, contaminating the main product, are formed.

4. (b) VO and VF_2 have the coordination lattice of the NaCl and TiO (rutile) type respectively. The lattice of VCl_2 and $V(OH)_2$ is lamellar (CdI type), consisting of octahedral unit cells.

5. (a) See Appendix 14.

(b) $[V(OH_2)_6]SO_4 \cdot H_2O$, $M_2[V(OH_2)_6]\,[SO_4]_2$; the colour is violet of differen shades.

8. (b) V_2O_3 and VF_3 are coordination crystals of the Al_2O_3 and ReO_3 struc ture type. VCl_3 has the lamellar lattice ($FeCl_3$ type).

10. (a) Due to increased oxidation state of V and, hence, due to the in creased value of Δ (see Appendix 12).

11. (c) It can be explained by the decreased contrapolarizing action of th ion in the outer sphere due to its increased dimensions.

12. The coordination numbers of V(IV) with respect to O and Cl are 6 and 4 VO_2(c) has the TiO_2 type lattice. VCl_4 is a liquid under normal condition (m.p. —26 °C) and consists of VCl_4 molecules.

21. 89.5 kJ/mol V_2O_5.

(b) 236 °C.

25. (b) It can be explained by the higher strength of the bonds Nb—Nb and Ta—Ta as compared with the bond V—V.

Chapter 11

d-Elements of Group VI

2. See Part Two, Chap. 9, Problem 2.

4. (a) The chemical activity decreases in the series Cr-Mo-W which is mainly due to the increasing bond energy in this series.

(c) 4*d*- and 5*d*-elements are characterized by high oxidation states which are stabilized in fluorine and oxoanion complexes.

6. (a) In accordance with the Jahn-Teller effect, unsymmetric filling of σ^*_d-orbitals with electrons distorts octahedral complex. The bond effected by $(\sigma_{x^2-y^2})^2$-electrons turns to be shorter and stronger than the bond effected by $(\sigma_{z^2})^2\,(\sigma^*_{z^2})^1$-electrons.

The structure of $CrCl_2$ is lamellar. The layers are formed by octahedral unit cells $CrCl_6$. The octahedra are distorted tetragonally: the bonds in the equatorial plane (*xy*) are shorter (0.239 nm) than the axial bonds (along the *z* axis) (0.290 nm).

7. See Appendix 14.

8. (d) The strong reducing power of $Cr(OH_2)_6^{2+}$ can be explained by the easiness with which the configuration $(\pi_d^{non})^3\,(\sigma^*_{d_{z^2}})^1$ changes to $(\pi_d^{non})^3$ due to the loss of the antibonding electron. Moreover, the activity of the ion $Cr(OH_2)_6^{2+}$ is associated with its unsymmetric structure.

9. (b) Dihalides of Mo and W, unlike dihalides of Cr, are cluster compounds. Cluster halides are characteristic of 4*d*- and 5*d*-elements of groups V-VIII, and are not characteristic of 3*d*-elements. This fact can be explained by the higher bond energy of simple substances of 4*d*- and 5*d*-elements as compared with 3*d*-elements. The tendency to use all their valency electrons in the formation of chemical bond, which is characteristic of 4*d*- and 5*d*-elements, is normally realized through transition to a higher oxidation state. For low oxidation states, this tendency is realized through the formation of the Me—Me bonds, i.e. through the formation of cluster compounds.

12. (b) —273 kJ/mol $Ca(CrO_2)_2$; —818 kJ/mol $Cr_2(SO_4)_3$.

16. The Cr^{2+}—OH_2 bond in $Cr(OH_2)_6^{2+}$ is weaker than the bond Cr^{3+}—OH_2 in $Cr(OH_2)_6^{3+}$. The complex $Cr(OH_2)_6^{2+}$ is distorted tetragonally and is therefore labile, i.e. kinetically more active than non-distorted kinetically inert $Cr(OH_2)_6^{3+}$

17. (b) The shift of the absorption maxima is due to decreased value of Δ

(c) As the H_3N molecules are replaced by the H_2O molecules Δ decreases:

	$Cr(NH_3)_6^{3+}$	$Cr(NH_3)_5(OH_2)^{3+}$	$Cr(NH_3)_4(OH_2)_2^{3+}$	$Cr(NH_3)_3(OH_2)_3^{3+}$
Δ, kJ/mol	258	—	241	221
Colour . . .	yellow	orange-yellow	orange-red	pale-red

	$Cr(NH_3)_2(OH_2)_4^{3+}$	$Cr(NH_3)(OH_2)_5^{3+}$	$Cr(OH_2)_6^{3+}$
Δ, kJ/mol	224	—	208
Colour . . .	red-violet	red-violet	violet

19. See Part One, Chap. 7, Problem 17.
20. See [1], Fig. 233.
21. See Part Two, Chap. 10, Problem 11.
26. (b) —46.5 kJ/mol Cr_2O_3: 135.0 kJ/mol MoO_2; 230.2 kJ/mol WO_2; the thermal stability increases and the oxidizing activity decreases.
27. (b) Acid medium decreases the oxidation state of *d*-elements since cation aquo complexes are formed. Alkaline medium promotes formation of anion oxo-complexes, i.e. facilitates the increase of the oxidation state of *d*-elements.

Chapter 12

d-Elements of Group VII

2. See Part Two, Chap. 9, Problem 2.
6. (b) MnO and MnS are coordination crystals of the NaCl structure type. MnF_2 are coordination crystals of the TiO_2 (rutile) type. $MnCl_2$ and $Mn(OH)_2$ are lamellar structure crystals (CdI_2 type).
8. (b) $[Mn(OH_2)_6]\,[NO_3]_2$, $[Mn(OH_2)_6](ClO_4)_2$, $[(H_2O)_4Mn(SO_4)_2Mn(OH_2)_4]$.
12. (b) Structural type of rutile.
22. (a) The changed stability of compounds is explained by the increased strength of the EO bond in EO_4^- in the series Mn-Tc-Re.
25. The role of π-bonding increases with the oxidation state of Mn in the MnO_4^{n-} ions.
26. The ability to form anion complexes and their stability increase with oxidation state of Mn which accounts for the increased acid properties of binary compounds.

Chapter 13

d-Elements of Group VIII. The Iron Subgroup

2. (b) It is known that $\Delta G = -nFE$, $\Delta G = \Delta H - T\Delta S$. If the entropy change is disregarded, then E of the process

$$M(c) \rightarrow M^{n+}(sln) + ne^-$$

depends on ΔH_f of the metal M^{n+} ion (sln). In accordance with the cycle

$$\begin{array}{ccc} M(c) & \xrightarrow{\Delta H_{subl}} & M(g) \\ \Delta H_f \downarrow & & \downarrow \Delta H_{ion} \\ M^{n+}(sln) & \xleftarrow{\Delta H_{hydr}} & M^{n+}(g) + ne^- \end{array}$$

$$\Delta H_f = \Delta H_{subl} + \Delta H_{ion} + \Delta H_{hydr}$$

According to the table

	Fe	Ru	Os
ΔH_{subl}, kJ/mol	405	670	732
$-\Delta H_{hydr}$ E^{2+}, kJ/mol	1925	1875	1858
ΔH_{ion} ($E \rightarrow E^{2+}$), kJ/mol	2322	2327	2460

the bond energy in the series Fe-Ru-Os, and hence the heat of sublimation, increase to a greater extent than ΔH_{hydr} and ΔH_{ion} are changed. Therefore, in the series Fe-Ru-Os, the positive value of the electrode potential of the system M^{2+}/M increases, and the chemical activity of the simple substances in solution decreases.

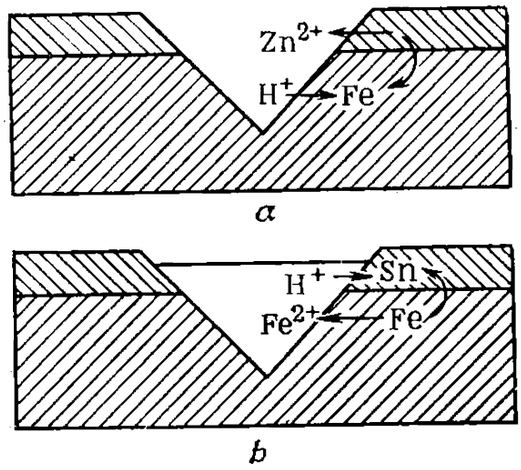


Fig. 103. Diagram of corrosion of zinc- and tin-plated iron.

4. The regularity of corrosion of iron is shown in Fig. 85*c*, and of ruthenium and osmium in Fig. 85*a*.

5. The concentration of the ion OH_3^+ increases with growing concentration of H_2SO_4 and this accelerates the rate of iron dissolution. At concentrations of sulphuric acid over 60 per cent, the reactivity of iron sharply decreases because iron is passivated due to formation of an oxide film on its surfaces. The tendency of iron to passivation in concentrated sulphuric acid makes it possible to transport the acid in steel tank cars.

6. When a protective coat is damaged, a more active metal is dissolved and hydrogen is liberated on a less active metal. In the case of zinc-plated iron (Fig. 103*a*), the protective zinc coat is dissolved while corrosion of iron is inhibited. If iron is coated with tin, the more active iron is destroyed at the site of the damaged coat while tin is not chemically affected (Fig. 103*b*).

10. The frequency of valency oscillations in a free CO molecule is 2143 cm^{-}. The lowered $\tilde{\nu}_{CO}$ in carbonyls indicates decreased order of the C—O bond in the complex formation. The stronger the dative interaction M—C, the more significant the decrease in the C—O oscillation frequency.

11. (a) The crystals FeO and FeF_2 have the coordination structure (NaCl and TiO_2 types). $FeCl_2$ and $Fe(OH)_2$ have the lamellar structure (CdI_2 type).

13. (a) NH_4^+, $Fe(OH_2)_6^{2+}$, SO_4^{2-}.

17. The crystals FeF_3 and Fe_2O_3 have the coordination structure of the ReO_3 and Al_2O_3 type. $FeCl_3$ has the lamellar structure.

19. (a) See Part One, Chap. 7, Problem 16.

21. (a) The complex $Fe(CN)_3^{3-}$ is more stable. The bond Fe—CN is strengthened at the expense of π-bonds formed by the dative mechanism (with the involvement of π_d-electrons of Fe(III) and vacant π*-orbitals of the CN^- ion).

24. (a) $[\sigma]^8[\pi]^{10}[\pi^{non}]^6[\pi^*]^2$.

Chapter 14

d-Elements of Group VIII. The Cobalt Subgroup

2. (a) See Part Two, Chap. 9, Problem 2.
(b) See Part Two, Chap. 13, Problem 2(b).

4. See Part Two, Chap. 13, Problem 10.

6. (a) 500 nm. See Appendix 14.

7. (c) Anion complexes of cobalt(II) have tetrahedral structure. The values of Δ are close in magnitude (see Appendix 12). Wavelengths of the maximum absorption of these complexes are also similar (600 and 673 nm for $Co(CNS)_4^{2-}$

and $CoCl_4^{2-}$, respectively). The tetrahedral complexes of Co(II) are therefore of similar colour.

8. (c)

	$CoCl_2 \cdot 6H_2O$	$CoCl_2 \cdot 4H_2O$	$CoCl_2 \cdot 2H_2O$	$CoCl_2$
Crystal lattice	insular	insular	chain	lamellar
Unit cell	$Co(OH_2)_4Cl_2$	$Co(OH_2)_4Cl_2$	$Co(OH_2)_2Cl_4$	$CoCl_6$
Δ, kJ/mol	104	104	96	88

9. $Co(OH)_2(c) + 1/4\ O_2(g) + 1/2 H_2O(l)$, $\Delta G^\circ_{298} = -22$ kJ/mol $Co(OH)_2$

$$Co(OH)_3 + e^- = Co(OH)_2 + OH^-, \quad E^\circ = 0.17 \text{ V}$$

$$O_2 + 2H_2O + 4e^- = 4OH^-, \quad E^\circ = 0.401 \text{ V}$$

11. Complexes with the electron configuration $[\sigma]^{12}[\pi_d^{non}]^6$ are characterized by thermodynamic and kinetic stability.

Chapter 15

d-Elements of Group VIII. The Nickel Subgroup

2. See Part Two, Chap. 9, Problem 2, Chap. 13, Problem 2.

b) Continuous solid solutions are formed in the systems Ni-Pd, Pd-Pt. The interacting pairs of metals, Ni and Pd, and Pd and Pt have face-centered cubic lattice and similar atomic radii and ionization energies.

5. (a) See, [1] Fig. 239. For a given complexing agent and the same ligands, the value of the parameter of splitting Δ of a square complex is higher than of an octahedral one: $\Delta_{square} = 1.3\Delta_{oct}$. Of the three components of Δ (Δ_1, Δ_2, Δ_3) of the square complex, the value Δ_1 is much higher than Δ_2 and Δ_3 and is approximately $0.8\Delta_{oct}$. It should be remembered that the parameters of splitting of similar complexes of *d*-elements of the fifth and sixth periods are higher than for *d*-elements of the fourth period. Thus, with the configuration d^8 for 4*d*- and 5*d*-elements, the filling of π^*_{xz}, π^*_{yz}, $\sigma^*_{z^2}$ and π^*_{xy} orbitals of the square complex is more advantageous energetically than of π^{non}_{xz}, π^{non}_{yz}, π^{non}_{xy}, $\sigma^*_{x^2-y^2}$ and $\sigma^*_{z^2}$ orbitals of the octahedral complex.

6. (a) According to Fig. 91 and Appendix 14, the complex $Ni(OH_2)_6^{2+}$ absorbs the purple component of the visible spectrum ($\lambda = 740$ nm) and its colour is green. The ion $Ni(NH_3)_6^{2+}$ absorbs the yellow-green component of the light ($\lambda = 571$ nm) and its colour is violet. The complex $Ni(en)_3^{2+}$ absorbs green light ($\lambda = 545$ nm) and is purple. See Appendix 12.

(c) $[Ni(OH_2)_6]F_2$, $[Ni(OH_2)_6](NO_3)_2$, $[Ni(OH_2)_6]CO_3$, $[Ni(OH_2)_6]SiF_6$, $[Ni(OH_2)_6]SO_4 \cdot H_2O$.

7. (a) $(NH_4)_2[Ni(OH_2)_6](SO_4)_2$.

8. $\Delta G^\circ_{303} = -51.6$ kJ/mol.

9. (a) $\Delta G^\circ_{303} = -53.6$ kJ/mol $Ni(en)_3^{2+}$.

(b) $\Delta S^\circ_{303} = 94.1$ J/mol deg.

(c) The chelate complex is more stable because of the entropy effect.

13. (b) See Problem 5.

15. See Part Two, Chap. 8, Problem 6.

Chapter 16

d-Elements of Group I

8. See Part Two, Chap. 11, Problem 6.

(b) The splitting energy increases in the transition from $Cu(OH_2)_6^{2+}$ ($\Delta = 150$ kJ/mol) to $Cu(NH_3)_6^{2+}$ ($\Delta = 180$ kJ/mol). This results in an even greater

tetragonal distortion of the octahedral complex and, hence, in an even greater weakening of the bonds between the ion Cu^{2+} and the molecules of H_3N (in the axial position). The ion $[Cu(NH_3)_4(OH_2)_2]^{2+}$ is therefore more stable than the ion $[Cu(NH_3)_6]^{2+}$.

10. (c) The energy of splitting of the complex ion $Cu(OH_2)_6^{2+}$ ($\Delta = 150$ kJ/mol) is lower than of the ion $[Cu(NH_3)_4(OH_2)_2]^{2+}$ ($\Delta = 161$ kJ/mol) but is higher than of the ion $CuCl_4^{2-}$ ($\Delta = 53$ kJ/mol). The conversion of the light blue ion $Cu(OH_2)_6^{2+}$ into the dark blue ion $[Cu(NH_3)_4(OH_2)_2]^{2+}$ corresponds to the shift in the absorption of the electromagnetic radiation towards shorter wavelengths, while the conversion into the green ion $CuCl_4^{2-}$, towards longer wavelengths.

16. See Appendices 19 and 21.

21. See Part Two, Chap. 15, Problem 5.

Chapter 17

d-Elements of Group II

10. 121 kJ/mol $Zn(NO_3)_2 \cdot 2H_2O$; 165 kJ/mol $Cd(NO_3)_2 \cdot 2H_2O$

14. $E(OH)_2 + 2H^+ = E^{2+} + 2H_2O$; $\Delta G^\circ_{298} = -66$ kJ/mol $Zn(OH)_2$; $\Delta G^\circ_{298} = -78$ kJ/mol $Cd(OH)_2$

$E(OH)_2 + 2OH^- = E(OH)_4^{2-}$; $\Delta G^\circ_{298} = -35$ kJ/mol $Zn(OH)_2$; $\Delta G^\circ_{298} = +34$ kJ/mol $Cd(OH)_2$

Appendices

Appendix 1

The International System of Units

Quantity	Symbol	Name of unit	Unit
		Base Units	
length	l	metre	m
mass	m	kilogram	kg
time	t	second	s
electric current	I	ampere	A
temperature	T	kelvin	K
luminous intensity	I	candela	cd
amount of substance	n	mole	mol
		Derived Units	
wave number	σ, ν	minus first power of metre	m^{-1}
wavelength	λ	metre	m
density	ρ	kilogram per cu. m.	kg/m^3
relative density	d	—	—
pressure	p	pascal	Pa
quantity of electricity	Q	coulomb	C
electric dipole moment	μ	coulomb-metre	C·m
electric potential difference	V	volt	V
electromotive force	E	volt	V
work	W (A)	joule	J
quantity of heat	Q	joule	J
internal energy	U	joule	J
enthalpy	H	joule	J
Gibbs free energy	G	joule	J
heat capacity	C	joule by kelvin	J/K or J/deg
entropy of system	S	joule by kelvin	J/K or J/deg

Quantity	Symbol	Name of unit	Unit
proton number, atomic number	Z	—	—
neutron number	N	—	—
mass number	A	—	—
atomic mass	$m(X)$	kilogram	kg
Bohr magneton	μ_B	ampere-sq. m.	$A \cdot m^2$
bond energy	E	joule	J
relative atomic mass	A_r	—	—
relative molecular mass	M_r	—	—
molar mass	M	kilogram by mole	kg/mol
molar volume	V_m	cubic metre by mole	m^3/mol
electrolytic conductivity	σ	siemens by metre	S/m
molar electric conductance	Λ_m	siemens-sq. m. by mole	$S \cdot m^2/mol$

Appendix 2

Fundamental Physical Constants

Constant	Symbol	Value	Unit
Speed of light in vacuum	c	2.997925×10^8	$m \cdot s^{-1}$
Elementary charge	e	1.60210×10^{-19}	C
Avogadro constant (carbon scale)	N_A	6.02252×10^{23}	mol^{-1}
Rest mass:			
of electron	m_e	9.1091×10^{-31}	kg
of proton	m_p	1.67252×10^{-27}	kg
of neutron	m_n	1.67474×10^{-27}	kg
Faraday constant	F	9.64870×10^4	$C \cdot mol^{-1}$
Planck constant	h	6.6256×10^{-34}	J·s
Gas constant	R	8.314	$J \cdot mol^{-1} \cdot deg^{-1}$
Absolute zero	T_0	—273.15°C	
Atomic mass unit		1.66×10^{-27}	kg
Molar volume of ideal gas at STP (°C, 101,325 kPa)	V_0	22.41×10^{-3}	$m^3 \cdot mol^{-1}$

Appendix 3

Prefixes for Units in the International System

Prefix	Symbol	Power
tera	T	10^{12}
giga	G	10^9
mega	M	10^6
kilo	k	10^3
hecto	h	10^2
deca	da	10^1
deci	d	10^{-1}
centi	c	10^{-2}
milli	m	10^{-3}
micro	μ	10^{-6}
nano	n	10^{-9}
pico	p	10^{-12}

Orbital Radii of Atoms, nm
(Radii of maximum radial electron density distribution)

Atom	1s	2s	2p	Atom	4d	5s	5p
H	**0.053**			Rb		**0.229**	
He	**0.029**			Sr		**0.184**	
Li	0.019	**0.159**		Y	0.086	**0.169**	
Be	0.014	**0.104**		Zr	0.079	**0.159**	
B	0.011	0.0771	**0.078**	Nb	0.075	**0.159**	
C	0.009	**0.062**	0.060	Mo	0.070	**0.152**	
N	0.0078	**0.052**	0.049	Tc	0.065	**0.139**	
O	0.0068	**0.045**	0.041	Ru	0.062	**0.141**	
F	0.0060	**0.040**	0.036	Rh	0.059	**0.136**	
Ne	0.0054	**0.035**	0.032	Pd	0.057	—	
				Ag	0.054	**0.128**	
				Cd	0.050	**0.118**	
Atom	3s	3p		In	0.048	0.109	**0.138**
				Sn	0.046	0.103	**0.124**
				Sb	0.044	0.097	**0.119**
				Te	0.042	0.092	**0.111**
Na	**0.171**			I	0.040	0.087	**0.104**
Mg	**0.128**			Xe	0.039	0.084	**0.099**
Al	0.104	**0.131**					
Si	0.090	**0.107**					
P	0.080	**0.092**					
S	0.072	**0.081**					
Cl	0.066	**0.072**					
Ar	0.061	**0.066**					

Atom	3d	4s	4p	Atom	5d	6s	6p
K		**0.216**		Cs		**0.252**	
Ca		**0.169**		Ba		**0.206**	
Sc	0.054	**0.157**		La	0.108	**0.191**	
Ti	0.049	**0.148**		Hf	0.083	**0.147**	
V	0.045	**0.140**		Ta	0.078	**0.141**	
Cr	0.043	**0.143**		W	0.075	**0.136**	
Mn	0.039	**0.128**		Re	0.071	**0.131**	
Fe	0.036	**0.123**		Os	0.070	**0.126**	
Co	0.034	**0.118**		Ir	0.067	**0.123**	
Ni	0.032	**0.114**		Pt	0.066	**0.122**	
Cu	0.031	**0.119**		Au	0.063	**0.119**	
Zn	0.029	**0.107**		Hg	0.060	**0.113**	
				Tl	0.058	0.106	**0.132**
Atom	4s	4p		Pb	0.056	0.101	**0.122**
				Bi	0.054	0.096	**0.129**
				Po	0.052	0.092	**0.121**
Ga	0.126	**0.096**		At	0.050	0.088	**0.115**
Ge	0.109	**0.089**		Rn	0.049	0.085	**0.109**
As	0.083	**0.100**					
Se	0.078	**0.092**					
Br	0.073	**0.085**					
Kr	0.069	**0.079**					

Atomic Radii

Given in the Table are 'metallic' atomic radii (in nm) found by halving the minimum interatomic distances in the crystalline structure of the simple substances with the coordination number 12. A correction should be introduced for other coordination numbers. Parenthesized are covalent radii.

For more detail see Boky, G. B., *Crystallochemistry*, Nauka, Moscow, 1971 (in Russian).

Periods	*Subgroups*																
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	(H)															H (0.030)	He 0,122
2	Li 0.155	Be 0.113										B 0.091	C 0.077	N (0.055)	O (0.055)	F (0.064)	Ne 0.160
3	Na 0.189	Mg 0.160										Al 0.143	Si 0.143	P (0.110)	S (0.104)	Cl (0.099)	Ar 0.192
4	K 0.236	Ca 0.197	Sc 0.164	Ti 0.146	V 0.134	Cr 0.127	Mn 0.130	Fe 0.126	Co 0.125	Ni 0.124	Cu 0.128	Zn 0.139	Ga 0.139	Ge 0.139	As 0.148	Se 0.160	Br (0.114)	Kr 0.198
5	Rb 0.248	Sr 0.215	Y 0.181	Zr 0.160	Nb 0.145	Mo 0.139	Tc 0.136	Ru 0.134	Rh 0.134	Pd 0.137	Ag 0.144	Cd 0.156	In 0.166	Sn 0.158	Sb 0.161	Te 0.170	I (0.133)	Xe 0.218
6	Cs 0.268	Ba 0.221	La 0.187	Hf 0.159	Ta 0.146	W 0.140	Re 0.137	Os 0.135	Ir 0.135	Pt 0.138	Au 0.144	Hg 0.160	Tl 0.171	Pb 0.175	Bi 0.182	Po	At	Rn
7	Fr 0.280	Ra 0.235	Ac 0.203															

Lanthanide Series	Ce 0.183	Pr 0.182	Nd 0.182	Pm	Sm 0.181	Eu 0.202	Gd 0.179	Tb 0.177	Dy 0.177	Ho 0.176	Er 0.175	Tm 0.174	Yb 0.193	Lu 0.174

Actinide Series	Th 0.180	Pa 0.162	U 0.153	Np 0.150	Pu 0,162

Ionic Radii

The tabulated ionic radii are given according to Belov and Boky (in nm). 0.136 nm. All values are given with reference to the coordination number numbers. Parenthesized are theoretically found values. The ionic charge is detail see Boky, G. B., *Crystallochemistry*, Nauka, Moscow, 1971 (in Russian).

Periods	Subgroups								
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	
1	(H)								
2	**Li** 1+ 0.068	**Be** 2+ 0.034							
3	**Na** 1+ 0.098	**Mg** 2+ 0.074							
4	**K** 1+ 0.133	**Ca** 2+ 0.104	**Sc** 3+ 0.083	**Ti** 2+ 0.078 3+ 0.069 4+ 0.064	**V** 2+ 0.072 3+ 0.067 4+ 0.061 5+ 0.040	**Cr** 2+ 0.083 3+ 0.064 6+ 0.035	**Mn** 2+ 0.091 3+ 0.070 4+ 0.052 7+ 0.046	**Fe** 2+ 0.080 3+ 0.067	**Co** 2+ 0.078 3+ 0.064
5	**Rb** 1+ 0.149	**Sr** 2+ 0.120	**Y** 3+ 0.097	**Zr** 4+ 0.082	**Nb** 4+ 0.067 5+ 0.066	**Mo** 4+ 0.068 6+ 0.065	**Tc**	**Ru** 4+ 0.062	**Rh** 3+ 0.075 4+ 0.065
6	**Cs** 1+ 0.165	**Ba** 2+ 0.138	**La** 3+ 0.104 4+ 0.090	**Hf** 4+ 0.082	**Ta** 5+ (0.066)	**W** 4+ 0.068 6+ 0.065	**Re** 6+ 0.052	**Os** 4+ 0.065	**Ir** 4+ 0.065
7	**Fr**	**Ra** 2+ 0.144	**Ac** 3+ 0.111						

Lanthanide Series	**Ce** 3+ 0.102 4+ 0.088	**Pr** 3+ 0.100	**Nd** 3+ 0.099	**Pm** 3+ (0.098)	**Sm** 3+ 0.097	**Eu** 3+ 0.097

Actinide Series	**Th** 3+ 0.108 4+ 0.095	**Pa** 3+ 0.106 4+ 0.091	**U** 3+ 0.104 4+ 0.088	**Np** 3+ 0.102 4+ 0.086	**Pu** 3+ 0.101 4+ 0.085	**Am** 3+ 0.100 4+ 0.085

The values are based on the ionic radius of O^{2-} which is assumed to be of 6 and the corresponding corrections are required for other coordination given in the left and the ionic radius in the right part of the box. For more

	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
							H 1− 0.136 1+ 0.000	He 0 0.122
			B 3+ (0.020)	C 4+ 0.020 4− (0.260)	N 3+ 5+ 0.015 3− 0.148	O 2− 0.136	F 1− 0.133	Ne 0 0.160
			Al 3+ 0.057	Si 4+ 0.039	P 3+ 5+ 0.035 3− 0.186	S 2− 0.182 6+ (0.029)	Cl 1− 0.181 7+ (0.026)	Ar 0 0.192
Ni 2+ 0.074	Cu 1+ 0.098 2+ 0.080	Zn 2+ 0.083	Ga 3+ 0.062	Ge 2+ 0.065 4+ 0.044	As 3+ 0.069 5+ (0.047) 3− 0.191	Se 2− 0.193 4+ 0.069 6+ 0.035	Br 1− 0.196 7+ (0.039)	Kr 0 0.198
Pd 4+ 0.064	Ag 1+ 0.113	Cd 2+ 0.099	In 1+ 0.136 3+ 0,092	Sn 2+ 0.102 4+ 0,067	Sb 3+ 0.090 5+ 0.062 3− 0.208	Te 2− 0.211 4+ 0.089 6+ (0.056)	I 1− 0.22 7+ (0.050)	Xe 0 0.218
Pt 4+ 0.064	Au 1+ (0.137)	Hg 2+ 0.112	Tl 1+ 0.136 3+ 0.105	Pb 2+ 0.126 4+ 0.076	Bi 3+ 0.120 5+ (0.074) 3− 0.213	Po	At	Rn

Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
3+ 0.094	3+ 0.089	3+ 0.088	3+ 0.086	3+ 0.85	3+ 0.085	3+ 0.081	3+ 0.080

Atomic Ionization Potential

Atomic No.	Element	I_1		I_2		I_3	
		kJ/mol	eV	kJ/mol	eV	kJ/mol	eV
1	H	1312.1	13.599	—	—	—	—
2	He	2372.3	24.59	5251	54.42	—	—
3	Li	520.2	5.39	7298	75.64	11812	122.4
4	Be	899.5	9.32	1757	18.21	14844	153.9
5	B	800.6	8.298	2427	25.16	3659	37.9
6	C	1086.4	11.26	2353	24.38	4619	47.9
7	N	1402.3	14.53	2856	29.60	4576	47.4
8	O	1313.9	13.62	3388	35.12	5296	54.9
9	F	1681.1	17.42	3376	34.99	6045	62.7
10	Ne	2080.7	21.57	3964	41.08	6130	63.5
11	Na	495.8	5.14	4564	47.30	6913	71.7
12	Mg	737.7	7.65	1451	15.04	7730	80.1
13	Al	577.6	5.986	1817	18.8	2744	28.4
14	Si	786.5	8.15	1577	16.34	3228	33.46
15	P	1011.8	10.49	1904	19.73	2910	30.16
16	S	999.6	10.36	2253	23.35	3380	35.0
17	Cl	1251.2	12.97	2296	23.80	3850	39.9
18	Ar	520.6	15.76	2666	27.63	3946	40.9
19	K	418.8	4.34	3070	31.82	4390	46.0
20	Ca	589.8	6.11	1145	11.87	4941	51.2
21	Sc	633.1	6.562	1235	12.80	2388	24.8
22	Ti	658	6.82	1310	13.58	2650	27.5
23	V	650.3	6.740	1372	14.21	2830	29.3
24	Cr	652.7	6.765	1592	16.50	2990	31.0
25	Mn	717.4	7.435	1509	15.64	3251	33.7
26	Fe	761.6	7.893	1561	16.18	2956	30.6
27	Co	759	7.87	1646	17.06	3231	33.5
28	Ni	736.7	7.635	1751	18.15	3392	35.2
29	Cu	745.4	7.726	1958	20.29	3554	36.8
30	Zn	906.4	9.394	1733	17.96	3830	39.7
31	Ga	578.7	6.09	1979	20.51	2962	30.7
32	Ge	762.2	7.90	1538	15.94	3301	34.2
33	As	947	9.82	1797	18.62	2734	28.3
34	Se	940.9	9.75	2045	21.19	3090	32.0
35	Br	1142	11.84	2103	21.8	3460	35.9
36	Kr	1350.8	14.0	2351	24.5	3560	36.9
37	Rb	403.0	4.18	2650	27.5	3930	40.0
38	Sr	549.4	5.69	1064	11.0	4210	43.6
39	Y	599.8	6.217	1181	12.24	1980	20.5
40	Zr	659.7	6.84	1267	13.13	2217	22.9
41	Nb	664.0	6.882	1382	14.32	2400	25
42	Mo	685	7.10	1558	16.15	2618	27.1
43	Tc	702	7.28	1472	15.26	3100	32
44	Ru	710.7	7.366	1617	16.76	2746	28.5
45	Rh	720.0	7.46	1744	18.08	2996	31.05
46	Pd	804.3	8.336	1875	19.43	3170	32.9
47	Ag	731.0	7.576	2073	21.49	3360	34.8
48	Cd	867.8	8.994	1631	16.9	3610	37.5
49	In	558.3	5.78	1820	18.9	2700	28.0
50	Sn	708.6	7.34	1411	14.6	2942	30.5

Continuation

Atomic No.	Element	I_1		I_2		I_3	
		kJ/mol	eV	kJ/mol	eV	kJ/mol	eV
51	Sb	834	8.64	1590	16.5	2440	25.3
52	Te	869.3	9.01	1790	18.6	3000	31
53	I	1008.4	10.45	1843	19.1	—	—
54	Xe	1170.4	12.13	2050	21.3	3100	32.1
55	Cs	375.7	3.89	2420	25.1	—	—
56	Ba	502.8	5.2	965.2	10.0	3600	37
57	La	538.1	5.577	1067	11.0	1850	19.2
58	Ce	528	5.5	1047	10.8	1880	19.5
59	Pr	523	5.42	1018	10.5	—	—
60	Nd	530	5.49	1034	10.7	—	—
61	Pm	535	5.55	1052	10.9	—	—
62	Sm	543	5.63	1068	11.1	—	—
63	Eu	546.5	5.66	1085	11.2	—	—
64	Gd	594	6.16	1170	12.1	—	—
65	Tb	564	5.85	1112	11.5	—	—
66	Dy	572	5.93	1126	11.7	—	—
67	Ho	581	6.02	1139	11.8	—	—
68	Er	589	6.10	1151	11.9	—	—
69	Tm	596.4	6.18	1163	12.0	—	—
70	Yb	603	6.25	1175	12.2	—	—
71	Lu	523.5	5.43	1340	13.9	—	—
72	Hf	720	7.5	1440	14.9	—	—
73	Ta	761	7.89	1560	16.2	—	—
74	W	770	7.98	1710	17.7	—	—
75	Re	760	7.88	1600	16.5	—	—
76	Os	820	8.5	1640	17	—	—
77	Ir	880	9.1	1640	17	—	—
78	Pt	860	8.9	1791	18.6	—	—
79	Au	890.2	9.226	1980	20.5	—	—
80	Hg	1007.1	10.438	1809.7	18.8	—	—
81	Tl	589.3	6.11	1971	20.4	—	—
82	Pb	715.6	7.42	1450	15.0	—	—
83	Bi	703.1	7.29	1615	16.7	—	—
84	Po	813	8.43	1870	19.4	—	—
85	At	890	9.2	1940	20.1	—	—
86	Rn	1037.1	10.75	—	—	—	—
87	Fr	384	3.98	—	—	—	—
88	Ra	509.3	5.28	979	10.1	—	—
89	Ac	490	5.1	1164	12.1	—	—
90	Th	590	6.1	1110	11.5	—	—
91	Pa	570	5.9	—	—	—	—
92	U	597	6.2	1120	11.6	—	—
93	Np	600	6.2	—	—	—	—
94	Pu	585	6.06	—	—	—	—
95	Am	578	5.99	—	—	—	—
96	Cm	588	6.09	—	—	—	—
97	Bk	608	6.30	—	—	—	—
98	Cf	620	6.4	—	—	—	—
99	Es	630	6.5	—	—	—	—
100	Fm	640	6.6	—	—	—	—
101	Md	650	6.7	—	—	—	—
102	(No)	660	6.8	—	—	—	—

Appendix 8

Electron Affinity *F* of Atoms
(Expressed by energy of ionization of negative ions E^-)

Atomic number	Element	*F*, kJ/mol	*F*, eV
1	H	72.76	0.75
2	He	—21.2	—0.22
3	Li	57.0	0.59
4	Be	—18.3	—0.19
5	B	28.9	0.30
6	C	122.5	1.27
7	N	—20.3	—0.21
8	O	141.8	1.47
9	F	332.7	3.45
10	Ne	—21.2	—0.22
11	Na	~33	~0.34
12	Mg	—21.2	—0.22
13	Al	48.2	0.5
17	Cl	351.4	3.61
19	K	48.2	0.5
35	Br	338.9	3.54
53	I	325.09	3.38

Appendix 9

Ionization Energy *E* and
Electron Affinity *F* of Molecules

Molecule	*I*, eV	$I\times10^{-2}$, kJ/mol	*F*, eV	$F\times10^{-2}$, kJ/mol
Br_2	10.56	10.19	2.5	2.41
C_2	11.4	11.0	—	—
CN	14.20	13.70	3.82	3.7
Cl_2	11.48	11.08	2.3	2.2
Cs_2	3.2	3.09	—	—
F_2	15.69	15.14	3.08	2.97
H_2	15.43	14.89	—3.58	—3.45
I_2	9.40	9.07	2.58	2.49
K_2	4.0	3.86	—	—
Li_2	5.0	4.82	—	—
N_2	15.58	15.03	$\leqslant$ —2.8	$\leqslant$ —2.7
Na_2	4.90	4.73	—	—
O_2	12.08	11.66	0.44	0.42
P_2	9.6	9.26	—	—
S_2	9.36	9.03	$\geqslant$ 2	1.93
Se_2	8.88	8.57	—	—
Te_2	8.29	8.0	—	—

Dissociation Energy (D_0) and Internuclear Distance (d) of Diatomic Molecules and Ions*

Molecule	D_0, kJ/mol	d, nm	Molecule	D_0, kJ/mol	d, nm
Ag_2	161	0.25	HCl	(431.6)	0.127
Al_2	172	0.247	HF	(565.7)	0.092
As_2	(385)	—	HI	(298.3)	0.161
Au_2	226	0.247	HO	(427.8)	0.097
B_2	276	0.159	He_2^+	230	0.108
Br_2	190.1	0.128	I_2	148.8	0.267
Br_2^+	316	—	I_2^+	250	—
Br_2^-	82	—	I_2^-	102	—
C_2	(605.0)	0.124	K_2	53.6	0.392
C_2^+	527	—	Li_2	99.0	0.267
C_2^-	696.8	—	Li_2^+	121	—
CN	801	0.117	N_2	(945.3)	0.1097
CN^+	439	—	N_2^+	842.7	0.118
CN^-	1003	0.114	N_2^-	744.8	0.125
CO	1070.3	0.128	NO	(631.6)	0.115
CO^+	805.4	—	NO^+	1046	0.106
Cl_2	(242.6)	0.199	Na_2	71.1	0.308
Cl_2^+	387.9	0.189	O_2	493.6	0.1207
Cl_2^-	120	—	O_2^+	642.3	0.112
Cs_2	38.0	0.458	O_2^-	394	0.132
Cu_2	197	0.222	P_2	(489.1)	0.1885
F_2	155	0.142	P_2^+	467	—
F_2^+	320	0.133	S_2	(425.5)	0.189
F_2^-	117	—	S_2^+	518	—
H_2	432.1	0.074	S_2^-	544	—
H_2^+	255.7	0.106	Se_2	305.2	0.216
H_2^-	15	—	Te_2	259	0.256
HBr	362.5	0.141			

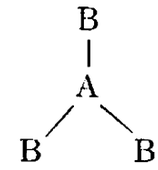
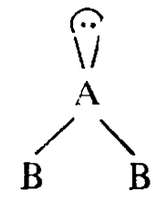
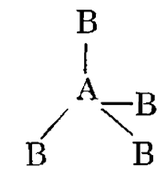
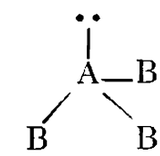
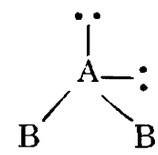
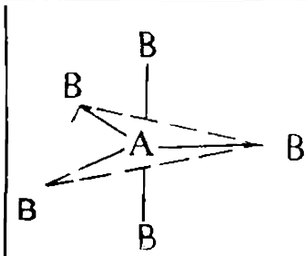
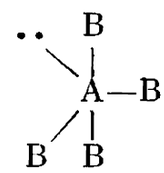
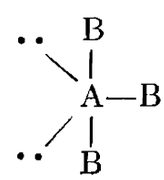
* Parenthesized are values at 298.15 K.

Appendix 11

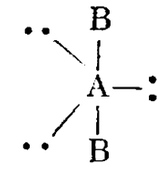
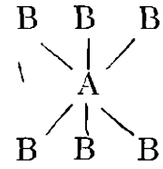
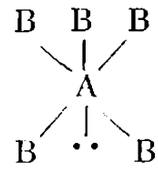
Arrangement of Valency σ-Electron Pairs of the Central Atom A and Spatial Configuration of Molecules (Complexes) AB_n

Number of σ-electron pairs of atom A			Molecule type	Spatial configuration of a molecule (complex)		Hybridization type describing the given configuration
total	bonding (without the number of A)	non-bonding				
2	2	0	AB_2	Linear	B—A—B	*sp*

Continuation

Number of σ-electron pairs of atom A			Molecule type	Spatial configuration of a molecule (complex)		Hybridization type describing the given configuration
total	bonding (without the number of A)	non-bonding				
3	3	0	AB_3	Triangular		sp^2
	2	1	AB_2	Angular		
4	4	0	AB_4	Tetrahedral		sp^3
	3	1	AB_3	Trigonal bipyramidal		
	2	2	AB_2	Angular		
5	5	0	AB_5	Trigonal bipyramidal		sp^3d
	4	1	AB_4	Distorted tetrahedral		
	3	2	AB_3	T-shaped		

Continuation

Number of σ-electron pairs of atom A			Molecule type	Spatial configuration of a molecule (complex)		Hybridization type describing the given configuration
total	bonding (without the number of A)	non-bonding				
5	2	3	AB_2	Linear		sp^3d
6	6	0	AB_6	Octahedral		sp^3d^2
	5	1	AB_5	Square pyramidal		

Appendix 12

Energy of electron splitting (Δ) and pairing (П) in octahedral complexes

Configuration of complexing ion	Ion	П, kJ/mol	Ligand	Δ, kJ/mol
d^2	V^{3+}	—	H_2O	212.4
d^3	V^{2+}	—	H_2O	140.8
	Cr^{3+}	—	H_2O	207.6
			H_3N	257.7
			F^-	181.3
			Cl^-	164.6
			Br^-	125.5
			CN^-	318.5
			CNS^-	212.6
d^4	Cr^{2+}	280.4	H_2O	165.8
			H_3N	205.2
d^5	Mn^{2+}	304.2	H_2O	101.4
			F^-	90.2
			Cl^-	89.5
			CN^-	308.9
			CNS^-	104.9
	Fe^{3+}	357.9	H_2O	163.4
			H_3N	202.8
			F^-	140.8
			Cl^-	130.6
			CN^-	417.6

Continuation

Configuration of complexing ion	Ion	П, kJ/mol	Ligand	Δ, kJ/mol
d^6	Fe^{2+}	209.9	H_2O	124.1
			H_3N	153.9
			F^-	106.2
			Cl^-	99.01
			Br^-	93.1
			CN^-	403.2
d^6	Co^{3+}	250.5	H_2O	217.0
			H_3N	273.2
			F^-	155.0
			CN^-	405.6
			en	277.9
d^7	Co^{2+}	304.2	H_2O	110.9
			H_3N	132.4
			F^-	95.4
			Cl^-	88.3
d^8	Ni^{2+}	—	H_2O	103.8
			H_3N	128.8
			en*	133.6
d^9	Cu^{2+}	—	H_2O	150.3
			H_3N	180.1
			en*	195.7
			F^-	128.8
			Cl^-	120.5

* en stands for ethylenediamine, $H_2NCH_2CH_2NH_2$.

13. The Theory of Colour

The perception of colour by the human eye results from the action of electromagnetic radiation with wavelengths occupying the range from about 400 to 760 nm ($\nu = 4 \times 10^{14}$-7.5×10^{14} cm^{-1}) on the optical nerve. Simultaneous action of the wavelengths in the entire visible range causes the perception of white, while narrow bands of radiation, or their combinations, which remain in the spectrum after extraction of some spectral bands, cause the perception of colour. The colour of an object is the result of the selective absorption of certain spectral regions and is characterized by the absorbed wavelength.

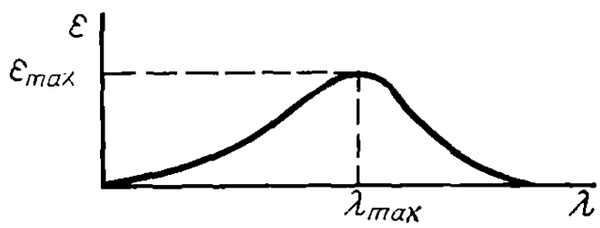


Fig. 104. Light absorption curve

It follows from the main equation of quantum theory $\Delta E = h\nu = hc/\lambda$ that the emission in the visible region of the spectrum corresponds to the energy of quanta (photons) of emission $E \approx 145$-290 kJ/mol (E being greater than 290 kJ/mol, the absorption occurs in the ultra-violet region and, E being smaller than 140 kJ/mol, the absorption occurs in the infra-red region of the spectrum). Said quanta of energy correspond to the transition of valency electrons from one energy level to another of many atoms and molecules.

The absorption of light by a substance can be described by an absorption curve. If absorption (ε) is plotted against wavelength (λ), the curve maximum on the axis of abscissas (λ_{max}) characterizes colour and is the measure of energy of the electron transition (excitation energy). The point ε_{max} on the axis of

ordinates characterizes the colour intensity and is a measure of probability of the electron transfer due to absorption of emitted quanta with wavelength λ_{max} (Fig. 104).

Appendix 14

Wavelengths of the Visible Spectrum and Colour

Absorbed wavelength, nm	Colour of absorbed radiation	Observed colour (complementary colour)
400-435	violet	greenish yellow
435-480	blue	yellow
480-490	green-blue	orange
490-500	blue-green	red
500-560	green	purple
560-575	yellow-green	violet
575-590	yellow	blue
590-605	orange	green-blue
605-730	red	blue-green
730-760	purple	green

Appendix 15

Thermodynamic Constants of Selected Substances

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
Ac (g)	—	—	187.93
Ac (c)	0	0	62.76
Ac_2O_3 (c)	−2050.16	−1958.11	133.89
Ag (g)	284.93	246.10	172.88
Ag (c)	0	0	42.55
Ag^+ (sln)	105.6	77.12	72.80
AgBr (c)	−100.7	−97.2	107.1
AgCl (c)	−127.1	−109.8	96.11
AgCN (c)	145.9	156.9	107.2
$Ag(CN)_2^-$ (sln)	—	−301.7	201.4
Ag_2CrO_4 (c)	−721.3	−635.0	217.6
AgF (c)	−206.0	−187.9	83.7
AgI (c)	−61.9	−66.4	115.5
$Ag(NH_3)_2^+$ (sln)	—	−17.57	246.27
$AgNO_3$ (c)	−124.6	−33.6	140.9
Ag_2O (c)	−31.1	−11.3	121.0
Ag_2S (c)	−32.8	−40.8	144.0
Ag_2SO_4 (c)	−717.2	−619.6	199.8
Al (g)	326.3	288.7	164.4
Al (c)	0	0	28.35
Al^{3+} (sln)	−530.0	−490.5	−301
$AlBr_3$ (c)	−513.4	−490.6	180.2
Al_4C_3 (c)	−209	−196	88.95
$AlCl_3$ (c)	−704.2	−628.6	109.3
$AlCl_3 \cdot 6H_2O$ (c)	−2693.4	−2262.8	318.2
AlF_3 (c)	−1510	−1432.0	66.48
AlF_6^{3-} (sln)	−2519.2	−2276.4	24
AlH_3 (c)	−11.4	46.4	30.0
AlI_3 (c)	−308	−304	189.5
AlN (c)	−318	−287.4	20.2

Continuation

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
$Al(OH)_3$ (c)	−1315	−1157	70.1
$Al(OH)_4^-$ (sln)	−1507.5	−1307.5	89.7
Al_2O_3 (c)	−1676	−1582	50.92
AlSb (c)	−96.2	—	69.03
Al_2S_3 (c)	−723.4	−492.5	96
$Al_2(SO_4)_3$ (c)	−3442.0	−3101	239.2
Ar (g)	0	0	154.7
As (g)	288.7	142.2	175.1
As (grey, c)	0	0	36.6
$AsBr_3$ (c)	−197.5	−161.7	159.0
$AsCl_3$ (l)	−305.0	−268.4	212.5
AsF_3 (g)	−920.65	−907.7	289.0
AsF_5 (g)	−1236.8	−1172.5	—
AsH_3 (g)	66.4	−68.9	223.0
AsI_3 (c)	−58.2	−65.8	163.6
AsO_4^{3-} (sln)	−880	—648	—163
As_4O_6 (c)	−1331.6	−1178.8	245
As_2O_5 (c)	−924.9	−782.4	105.4
H_3AsO_3 (sln)	−741.2	−640.5	179.3
H_3AsO_4 (sln)	−902.5	−765.7	205.0
As_2S_3 (c)	−159	−158.0	163.6
At (g)	97.2	59.6	186.98
At_2 (g)	87.9	37.5	276.1
At^- (g)	−178.7	−202.5	175.4
Au (g)	365.25	325.6	180.41
Au (c)	0	0	47.40
$AuBr_3$ (c)	−53.5	−24.67	100.42
$AuBr_4^-$ (sln)	—	−159.41	313.8
AuCl (c)	−36.4	−14.6	85.17
$AuCl_2$ (c)	−118.4	−53.6	164.4
$AuCl_4^-$ (sln)	−322.4	−235.76	268.45
$Au(CN)_2^-$ (sln)	—	269.45	123.43
AuF_3 (c)	−348.53	−297.48	114.22
$Au(OH)_3$ (c)	−477.8	−349.8	121
Au_2O_3 (c)	−13.0	78.7	134.3
B (g)	544	517.6	163.3
B (c)	0	0	5.8
BBr_3 (c)	—	−237.5	228.5
BCl_3 (l)	−427.1	−387.2	206
BF_3 (g)	−1137.0	−1120.0	254.37
BF_4^- (sln)	−1572.6	−1483.0	176.4
B_2H_6 (g)	38.5	89.6	232
BN (c)	−252.8	−226.8	14.8
$B(OH)_4^-$ (sln)	−1345.0	−1153.7	101.1
B_2O_3 (c)	−1254	−1193.7	80.8
HBO_2 (c)	−795	−736.1	240.2
H_3BO_3 (c)	−1094.0	−968.8	88.74
B_2S_3	—	−238.1	106.3
Ba (g)	174.6	144.8	170.1
Ba (c)	0	0	67
Ba^{2+} (sln)	−538.0	−561.1	9.6
$BaBr_2$ (c)	−756.5	−732	150
$BaCO_3$ (c)	−1219	−1139	112.0

Substance	$\Delta H^\circ_{f.\,298}$, kJ/mol	$\Delta G^\circ_{f.\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
$BaCl_2$ (c)	−859.1	−811.4	126.0
$Ba(ClO_3)_2$ (c)	—	−556.9	234.3
$Ba(ClO_4)_2$ (c)	−858.98	−535.6	255.2
$BaCrO_4$ (c)	−1368	−1325.2	155.6
BaF_2 (c)	−1200	−1149	96.2
BaI_2 (c)	−605.4	−619	167
$Ba(NO_3)_2$ (c)	−991.0	−795.0	214
BaO (c)	−558.1	−528.4	70.3
BaO_2 (c)	−629.7	−587.9	65.7
$Ba(OH)_2$ (c)	−950	−886	124.0
$Ba_3(PO_4)_2$ (c)	−3969.2	−3951.4	355.6
BaS (c)	−460.5	−456	78.3
$BaSO_4$ (c)	−1465.0	−1353.0	132.0
$BaSiO_3$ (c)	−1590.1	−1525.9	109.6
Ba_2SiO_4 (c)	−2265.6	−2145.6	176.1
$BaTiO_3$ (c)	−1663.6	−1574.9	108.03
Be (g)	326.5	288.8	136.2
Be (c)	0	0	9.5
Be^{2+} (sln)	—	−381.2	−196.6
$BeBr_2$ (c)	−330	−354	103
Be_2C (c)	−90.8	−88.3	16.3
$BeCO_3$ (c)	−982	−944.7	67.29
$BeCl_2$ (c)	−494	−468	63
BeF_2 (c)	−1010	−941	45
BeH_2 (c)	125	115.7	173
BeI_2 (c)	−165	−210	130
BeO (c)	−598	−582	14.1
$Be(OH)_2$ (c)	−907	−818	55.6
$BeSO_4$ (c)	−1197	−1088	90
Bi (g)	207.1	159.6	186.9
Bi (c)	0	0	56.9
Bi^{3+} (sln)	81	91.9	−175
$BiCl_3$ (c)	−379.0	−313.1	172.0
$BiCl_4^-$ (sln)	—	−482.1	—
BiI_3 (c)	−108.9	−175.4	234.0
BiOCl (c)	−371.4	−231.2	102.6
Bi_2O_3 (c)	−577.8	−497.3	151
$Bi(OH)_3$ (c)	−711.8	−580.3	118
Bi_2S_3 (c)	−155.6	−152.9	200.4
$Bi_2(SO_4)_3$ (c)	−2554	−2583.3	—
Br (g)	111.8	82.4	186.9
Br^- (g)	−218.9	−238.7	163.4
Br^- (sln)	−131.2	−107.1	83.3
Br_2 (g)	30.9	3.1	245.5
Br_2 (l)	0	0	152.2
BrF (g)	−42.4	−57.7	228.9
BrF_3 (l)	−303.1	−242.9	178.1
BrF_5 (g)	−428.9	−350.3	319.2
BrO_3^- (sln)	−40.2	1.84	161.1
HBr (g)	−34.1	−51.2	198.6
HBrO (sln)	−112.97	−82.4	142.3
C (g)	712.5	669.7	157.99
C (diamond, c)	1.828	2.833	2.36

Continuation

Substance	$\Delta H^\circ_{f,298}$, kJ/mol	$\Delta G^\circ_{f,298}$, kJ/mol	S°_{298}, J/(mol·deg)
C (graphite, c)	0	0	5.74
CBr_4 (g)	79.5	66.94	230.12
CCl_4 (g)	-102.93	-60.63	309.74
CCl_4 (l)	-135.44	-64.7	214.6
CF_4 (g)	-933.7	-887.97	216.6
CH_4 (g)	-74.86	-50.79	186.19
CI_4 (g)	—	260.90	391.83
CN^- (sln)	151.2	171.6	96.4
CO (g)	-110.52	-137.14	197.54
$COCl_2$ (g)	-220.3	-266.9	283.9
COF_2 (g)	-634.71	-619.23	258.49
CO_2 (g)	-393.5	-394.38	213.68
CO_3^{2-} (sln)	-676.3	-528.1	-54.9
CS_2 (l)	88.7	64.4	151.0
HCN (l)	-109.6	-125.6	113.2
HCO_3^- (sln)	-691.1	-587.1	95.0
H_2CO_3 (sln)	-699.5	-619.2	187.4
Ca (g)	177.3	143.6	154.8
Ca (c)	0	0	41.63
Ca^{2+} (sln)	-542.96	-553.0	-55.2
Ca $(AlO_2)_2$ (c)	-2327.9	-2210.2	144.3
Ca $(BO_2)_2$ (c)	-2030.96	-1924.2	105.2
$CaBr_2$ (c)	-674.9	-656.1	130
$CaBr_2 \cdot 6H_2O$ (c)	-2507.9	-2118.9	410
CaC_2 (c)	-62.8	-67.8	70.3
$CaCO_3$ (calcite, c)	-1206.9	-1128.8	92.9
$CaCl_2$ (c)	-795	-750.2	113.6
$CaCl_2 \cdot 6H_2O$ (c)	-2599.6	-2198.9	285.1
$CaCrO_4$ (c)	-1380.0	-1308.76	133.89
Ca $(CrO_2)_2$ (c)	-2068.57	-1936.36	120.92
CaF_2 (c)	-1214.6	-1161.9	68.9
$CaHPO_4$ (c)	-1815.6	-1682.4	111.5
$CaHPO_4 \cdot 2H_2O$ (c)	-2405.2	-2156.2	189.6
CaH_2 (c)	-188.7	-149.8	42
CaI_2 (c)	-534.7	-529.0	142
$CaMoO_4$ (c)	—	-1446.4	—
Ca_3N_2 (c)	-431.8	368.6	105
CaO (c)	-635.5	-604.2	39.7
CaO_2 (c)	-651.7	-598	43.1
Ca $(OH)_2$ (c)	-986.6	-896.8	76.1
CaS (c)	-482.7	-477.7	56.5
$Ca_3 (PO_4)_2$ (c, β)	-4123.6	-3887.4	236.1
$CaSO_4 \cdot 0.5H_2O$ (c)	-1577.8	-1437.8	130.6
$CaSO_4 \cdot 2H_2O$ (gypsum, c)	-2023.98	-1798.7	194.3
$CaSiO_3$ (c)	-1636.0	-1550.8	81.98
$CaTiO_3$ (c)	-1654.77	-1569.41	—
$CaWO_4$ (c)	-1683.6	-1533.85	151.0
Cd (g)	111.92	77.37	167.65
Cd (c)	0	0	51.76
Cd^{2+} (sln)	-72.4	-77.65	-70.91
$CdBr_2$ (c)	-315.3	-295.8	138.83
$CdCO_3$ (c)	-754.6	-674.5	96.7
$CdCl_2$ (c)	-390.8	-343.2	115.27

Continuation

Substance	$\Delta H^{\circ}_{f,\,298}$, kJ/mol	$\Delta G^{\circ}_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
CdF_2 (c)	−700.4	−649.5	84
CdI_2 (c)	−204.2	−201.3	158.32
$Cd(NO_3)_2 \cdot 4H_2O$ (c)	−1653.2	−1236.5	393
$Cd(NO_3)_2 \cdot 2H_2O$ (c)	—	−748.94	—
CdO (c)	−260.0	−229.3	54.8
$Cd(OH)_2$ (c)	−561.5	−473.8	93.04
$Cd(OH)_4^{2-}$ (sln)	—	−755.0	—
CdS (c)	−156.9	−153.2	71.1
$CdSO_4$ (c)	−934.4	−823.9	123.05
Cl (g)	121.3	105.3	165.1
Cl^- (g)	−233.6	−239.9	153.2
Cl^- (sln)	−167.2	−131.4	56.54
Cl_2 (g)	0	0	222.9
ClF (g)	−49.9	−51.4	217.8
ClF_3 (l)	−157.7	−117.8	281.5
ClO^- (sln)	−110.1	−36.6	33
ClO_2 (g)	105	122.3	257.0
ClO_2^- (sln)	−69.0	14.6	100.4
ClO_3^- (sln)	−98.3	−2.6	163.2
ClO_4^- (sln)	−131.4	−10.8	180.7
Cl_2O (g)	75.7	93	266.2
Cl_2O_7 (g)	286.6	399.1	—
Cl_2O_7 (l)	251	—	—
HCl (g)	−91.8	−94.79	186.8
HCl (sln)	−166.9	−131.2	56.5
HClO (sln)	−124.3	−79.6	129
$HClO_4$ (l)	−34.5	84.31	188.0
Co (g)	424.68	380.16	179.41
Co (c)	0	0	30.04
Co^{2+} (sln)	−59.41	−53.55	−112.97
Co^{3+} (sln)	94.2	129.8	−285.21
$CoBr_2$ (c)	−223.84	−210.46	135.56
$CoCO_3$ (c)	−722.6	−651.0	—
$CoCl_2$ (c)	−325.5	−282.4	106.3
$CoCl_2 \cdot 6H_2O$ (c)	—	−1735.94	—
CoI_2 (c)	−102.1	−97.5	158.2
$Co(NH_3)_6^{2+}$ (sln)	—	−241.42	—
$Co(NH_3)_6^{3+}$ (sln)	—	−221.33	333.57
$Co(NO_3)_2$ (c)	−430.5	−230.5	192
$Co(NO_3)_2 \cdot 6H_2O$ (c)	−1655.6	—	—
CoO (c)	−239.3	−213.4	43.9
Co_3O_4 (c)	−879	−761.5	149.66
$Co(OH)_2$ (c)	−541.0	−456.1	82.0
$Co(OH)_3$ (c)	−730.53	−596.64	83.68
CoS (c)	−80.75	−82.84	67.36
$CoSO_4$ (c)	−868.2	−761.9	113.4
$CoSO_4 \cdot 7H_2O$ (c)	—	−2453.5	406.05
Cr (g)	397.5	352.64	174.22
Cr (c)	0	0	23.6
Cr^{2+} (sln)	−139.0	−183.4	41.9
Cr^{3+} (sln)	−236.1	−223.21	−215.6
$Cr(CO)_6$ (g)	−1005.8	−950.6	487.56
$Cr(CO)_6$ (c)	−1077.4	−970.4	314

Continuation

Substance	$\Delta H^\circ_{f,\ 298}$, kJ/mol	$\Delta G^\circ_{f,\ 298}$, kJ/mol	S°_{298}, J/(mol·deg)
$CrCl_2$ (c)	−395.4	−356.3	115.65
$CrCl_3$ (c)	−570.3	−500.7	124.7
CrF_3 (c)	−1159.7	−1089.3	94.14
CrF_6 (c)	—	−1090.06	—
CrN (c)	−123.4	−103.5	52.7
CrO_3 (c)	−585.76	−506.26	71.96
Cr_2O_3 (c)	−1140.6	−1059	81.2
CrO_4^{2-} (sln)	−882.2	−729.92	54
$Cr_2O_7^{2-}$ (sln)	−1491.9	−1305.4	270.57
CrO_2Cl_2 (l)	−598.73	−524.67	209.2
$Cr(OH)_2$ (c)	−677.81	−587.85	81.17
$Cr(OH)_3$ (c)	−999.98	−849.02	80.33
$Cr_2(SO_4)_3$ (c)	−3308	−2984	287.9
H_2CrO_4 (sln)	—	−765.3	—
Cs (g)	78.1	50.9	175.5
Cs (c)	0	0	84.35
Cs^+ (sln)	−247.7	−282.04	133.1
CsBr (c)	−394.6	−383.3	121
Cs_2CO_3 (c)	—	−1039	188.7
CsCl (c)	−433.0	−404.2	90.0
CsF (c)	−530.9	−505.4	79
CsH (c)	−49.9	−29.3	79
CsI (c)	−351.3	−333.5	130
$CsNO_3$ (c)	−494.2	−395.0	149.0
Cs_2O (c)	−317.6	−274.5	123.8
Cs_2O_2 (c)	−402.5	−327.2	118.0
CsOH (c)	−406.7	−362.3	93.3
CsO_2 (c)	−289.5	−211.3	—
Cs_2S (c)	−364	−326	146
Cs_2SO_4 (c)	−1642.6	−1300.0	205.9
Cu (g)	339.32	299.69	166.27
Cu (c)	0	0	33.15
Cu^+ (sln)	71.55	50.21	39.33
Cu^{2+} (sln)	66.99	65.61	−92.8
CuBr (c)	−103.5	−99.58	96.11
$CuBr_2$ (c)	−143	−131.1	146
$CuCO_3$ (c)	−595.4	−518.3	88
CuCl (c)	−137.3	−120.1	87.0
$CuCl_2$ (c)	−215.6	−171.4	108.1
$CuCl_2^-$ (sln)	−277.6	−244.59	210.95
$CuCl_2 \cdot 2H_2O$ (c)	−818.6	−660.1	190.6
CuF_2 (c)	−537.6	−487.8	68.6
CuI (c)	−68.0	−69.7	96.7
CuI_2 (c)	—	−11.71	163.18
$Cu(NH_3)_2^+$ (sln)	—	−30.5	117.74
$Cu(NH_3)_4^{2+}$ (sln)	—	−111.5	280.5
$Cu(NO_3)_2$ (c)	−305.34	−117.15	192.46
CuO (c)	−162	−129.4	42.63
Cu_2O (c)	−173.2	−150.5	92.93
$Cu(OH)_2$ (c)	−444.3	−359.4	84
$Cu(OH)_4^{2-}$ (sln)	−894.3	−658.2	43.34
$(CuOH)_2CO_3$ (c)	−1051	−909.9	211.6
CuS (c)	−53.1	−53.6	66.5

Continuation

Substance	$\Delta H^\circ_{f,\ 298}$, kJ/mol	$\Delta G^\circ_{f,\ 298}$, kJ/mol	S°_{298}, J/(mol·deg)
Cu_2S (c)	−79.5	−86.3	121
$CuSO_4$ (c)	−770.9	−661.8	109
$CuSO_4 \cdot 5H_2O$ (c)	−2279.4	−1879.9	300
F (g)	79.5	62.4	158.7
F^- (g)	−259.7	−266.6	145.5
F^- (sln)	−331.7	−277.9	−13.8
F_2 (g)	0	0	202.9
HF (g)	−270.9	−272.8	173.7
HF (sln)	−320.08	−296.86	—
HF_2^- (sln)	−642.3	−576.7	113.6
Fe (g)	416.31	370.67	180.38
Fe (c)	0	0	27.15
Fe^{2+} (sln)	−87.17	−78.96	−130.96
Fe^{3+} (sln)	−46.39	−4.52	−309.17
$FeBr_2$ (c)	−251.4	−239.6	140
$FeBr_3$ (c)	−269	−246	184
Fe_3C (c)	25	18.8	108
$Fe(CN)_6^{3-}$ (sln)	635.13	803.75	267.78
$Fe(CN)_6^{4-}$ (sln)	530.11	769.44	92.05
$FeCO_3$ (c)	−738.15	−665.1	95.4
$Fe(CO)_5$ (l)	−764.0	−695.2	338
$FeCl_2$ (c)	−341.75	−302.35	118.0
$FeCl_3$ (c)	−396.23	−340.16	145.6
FeO (c)	−264.8	−244.3	60.75
Fe_2O_3 (c)	−822.2	−740.3	87.4
Fe_3O_4 (c)	−1117.1	−1014.2	146.2
$Fe(OH)_2$ (c)	−561.7	−479.7	88
$Fe(OH)_4^{2-}$ (sln)	—	−770.4	—
$Fe(OH)_3$ (c)	−826.6	−699.6	105
FeS (c)	−100.4	−100.8	60.29
FeS_2 (pyrite, c)	−163.2	−151.8	52.93
$FeSO_4$ (c)	−929.47	−825.54	121.04
$FeSO_4 \cdot 7H_2O$ (c)	−3016	−2512	409.1
$Fe_2(SO_4)_3$ (c)	−2584	−2253	282.8
$FeSiO_3$ (c)	−1195.8	−1118.3	93.99
$FeTiO_3$ (ilmenite, c)	−1253.95	−1173.19	142.67
Ga (g)	271.7	233.2	—
Ga (c)	0	0	41.1
Ga^{3+} (sln)	−215.8	−161.78	−327.6
$GaCl_3$ (c)	−524.7	−492.8	133.4
GaF_3 (c)	—	−941.4	83.7
Ga_2O_3 (c)	−1089	−998.2	—
$Ga(OH)_3$ (c)	−1014.6	−831.78	84.9
$Ga(OH)_6^{3-}$ (sln)	—	−1431.0	—
GaP (c)	−121.7	—	—
Ga_2S_3 (c)	−569	—	—
GaSb (c)	−41.5	−38.2	80.8
Ge (g)	376.5	335.8	167.7
Ge (c)	0	0	31.3
$GeCl_4$ (g)	−504.6	−466.0	347.7
$GeCl_4$ (l)	−569	−497	251.0
GeF_4 (g)	−1190	−1150	303
GeH_4 (g)	90.8	113.2	217.1

Continuation

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
Ge_2H_6 (g)	159.4	—	—
GeO (c)	−255	−226.8	50.2
GeO_2 (c, I)	−554.7	−500.8	55.27
GeS (c, I)	−70.09	−70.97	65.98
GeS_2 (c)	−38.38	−39.9	78.28
GeSe (c)	−82.4	−84.0	79.0
H (g)	217.98	203.3	114.6
H^+ (g)	1536.2	1516.99	108.8
H^+ (sln)	0	0	0
H_2 (g)	0	0	130.52
He (g)	0	0	126.04
Hf (g)	702.9	656.89	186.77
Hf (c)	0	0	43.55
HfC (c)	−217.15	−205.6	40.08
$HfCl_4$ (c)	−990	−901	191
HfF_4 (c)	−1930	−1830	113
HfO_2 (c)	−1117.5	−1061.1	59.33
$Hf(OH)_4$ (c)	—	−361.89	—
Hg (g)	61.3	31.85	174.85
Hg (l)	0	0	75.90
Hg^{2+} (sln)	173.58	164.79	−25.17
Hg_2^{2+} (sln)	171.87	153.70	82.24
$HgBr_2$ (c)	−169.9	−155.5	179.8
Hg_2Br_2 (c)	−207.1	−181.3	217.7
$HgCO_3$ (c)	−553.29	−468.61	184.1
$HgCl_2$ (c)	−228.2	−180.9	140.02
Hg_2Cl_2 (c)	−265.1	−210.8	192.76
HgI_2 (c)	−105.4	−103.05	184.05
$Hg(NO_3)_2$ (c)	−226	—	—
$Hg(NO_3)_2 \cdot 2H_2O$ (c)	—	−563.6	—
HgO (c, red)	−90.9	−58.6	70.29
Hg_2O (c)	−91.3	−55.4	130.2
HgS (c, cinnabar)	−59.0	−51.4	82.4
$HgSO_4$ (c)	−707.9	−590.0	136.4
Hg_2SO_4 (c)	−744.65	−627.45	200.7
I (g)	106.3	69.5	178.8
I^- (g)	−195	−221	167.4
I^- (sln)	−55.9	−51.7	109.4
I_2 (g)	62.43	19.37	260.59
I_2 (c)	0	0	116.15
ICl (g)	17.41	−5.81	247.4
ICl_3 (c)	−88.3	−22.1	167.2
IF (g)	−125	−127.1	235.9
IF_5 (g)	−834.3	−763.9	328.9
IO_3^- (sln)	−230.1	−135.6	115.9
HI (g)	26.57	1.78	206.48
HI (sln)	−55.2	−51.5	111.3
H_5IO_6 (c)	−761.5	—	—
In (g)	—	203.5	173.7
In (c)	0	0	57.82
In^{3+} (sln)	−182.4	−98.4	−253.7
InAs (c)	−25.9	−24.2	41.0
InCl (c)	−186.2	−164.0	95.0

Continuation

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
$InCl_3$ (c)	−537.2	−460	138
In_2O_3 (c)	−925.9	−831.9	107.9
$In(OH)_3$ (c)	−760.0	−761.6	106.7
InP (c)	88.7	76.99	31.1
$In_2(SO_4)_3$ (c)	−2725.5	−2385.7	302.1
InSb (c)	−15.35	−14.1	88.3
Ir (g)	627.6	580.77	178.4
Ir (c)	0	0	35.48
$IrCl_3$ (c)	−242.7	−198.7	150.6
IrF_6 (g)	−544	−458.7	357.7
IrO_2 (c)	−243	−188.4	59
IrS_2 (c)	−125.6	—	105.51
K (g)	89.16	60.67	160.23
K (c)	0	0	71.45
K^+ (sln)	−251.2	−281.3	102.5
$KAg(CN)_2$ (c)	—	35.9	142.2
$KAlH_4$ (c)	−166.5	−99.5	128.8
KBF_4 (c)	−1881.5	−1778.2	50.2
KBH_4 (c)	−948.8	−159.4	106.2
$K_2B_4O_7$ (c)	−3334.2	−2998.8	187.4
KBr (c)	−392.5	−378.8	95.85
$KBrO_3$ (c)	−332.2	−243.5	149.2
KCN (c)	−112.5	−103.9	137.03
K_2CO_3 (c)	−1146.1	−1059.8	156.32
KCl (c)	−435.9	−408.0	82.56
$KClO_3$ (c)	−391.2	−289.9	142.97
$KClO_4$ (c)	−430.1	−300.4	151.0
K_2CrO_4 (c)	−1382.8	−1286.0	193.3
$K_2Cr_2O_7$ (c)	−2033.0	−1866	291.2
KF (c)	−567.4	−537.7	66.60
KH (c)	−63.4	−34.0	50.2
$KHCO_3$ (c)	−959.3	−860.6	128.7
KHF_2 (c)	−928.45	−860.45	104.6
KI (c)	−327.6	−324.1	110.79
KIO_3 (c)	−508.4	−425.5	151.46
KIO_4 (c)	−464.9	−391.2	157.7
$KMnO_4$ (c)	−813.4	−713.8	171.71
K_2MnO_4 (c)	−1184.07	—	—
KN_3 (c)	1.38	77.0	86.0
KNO_2 (c)	−370.3	−218.6	117
KNO_3 (c)	−493.2	−393.1	132.93
KOH (c)	−425.8	−380.2	79.32
KOH (sln)	−477.3	−440.5	91.6
KO_2 (c)	−280	−209	46.9
K_2O (c)	−363.2	−322.1	94.1
K_2O_2 (c)	−495.8	−429.8	113.0
K_2O_4 (c)	−562.8	−416.7	93.7
$K_2[PtCl_6]$ (c)	—	−1037.2	329.6
$KReO_4$ (c)	−1100.3	−995.7	167.7
K_2S (c)	−428.4	−404.2	111.3
$K_2SO_3 \cdot 2H_2O$ (c)	−1116.7	−1025	156.5
K_2SO_4 (c)	−1433.7	−1316.4	175.7
$K_4[Fe(CN)_6] \cdot 3H_2O$ (c)	−1423.8	−1097.5	598

Continuation

Substance	$\Delta H^{\circ}_{f,\ 298}$, kJ/mol	$\Delta G^{\circ}_{f,\ 298}$, kJ/mol	S°_{298}, J/(mol·deg)
$K_3[Fe(CN)_6]$ (c)	−173.2	−51.9	420.1
K_2TiO_3 (c)	−1609.17	—	237.23
Kr (g)	0	0	164
La (g)	416.73	379.35	182.3
La (c)	0	0	57.3
$LaCl_3$ (c)	−1070.7	−1028.8	144.3
La_2O_3 (c)	−1793.1	−1705.8	128.4
$La_2(SO_4)_3$ (c)	−3932.1	−3598.2	—
Li (g)	160.5	127.4	139.6
Li (c)	0	0	28.6
$LiAlH_4$ (c)	−117	−48.4	87.9
LiBr (c)	−350.3	−338.9	66.9
LiCl (c)	−408.3	−384.0	59.3
LiF (c)	−612.1	−584.1	35.9
$LiFeO_2$ (c)	−729.02	—	75.31
LiH (c)	−90.7	−68.5	20.0
LiI (c)	−271.1	−266.9	75.7
Li (OH) (c)	−487.2	−442.2	42.8
Li (OH) (sln)	−508.7	—	—
Li_2CO_3 (c)	−1215.6	−1132.4	90.37
$LiNO_3$ (c)	−482.3	−389.5	105
Li_2O (c)	−595.8	−562.1	37.89
Li_2SO_4 (c)	−1434.4	−1324.7	113
Mg (g)	146.4	111.9	148.5
Mg (c)	0	0	32.7
Mg^{2+} (sln)	−467	−455.1	138
$MgBr_2$ (c)	−517.6	—	117
$MgBr_2 \cdot 6H_2O$ (c)	−2407	−2054	397
$MgCO_3$ (c)	−1113	−1029.3	65.7
$MgCl_2$ (c)	−641.1	−591.6	89.8
MgF_2 (c)	−1113	−1071	57.2
$Mg(NO_3)_2 \cdot 6H_2O$ (c)	−2499.6	−2115.6	366
MgO (c)	−601.8	−569.6	26.9
$Mg(OH)_2$ (c)	−924.7	−833.7	63.14
$MgSO_4$ (c)	−1301.4	−1158.7	91.6
$MgSO_4 \cdot 7H_2O$ (c)	−3384	−2868	—
Mn (g)	279.2	236.98	173.6
Mn (c)	0	0	32.0
Mn^{2+} (sln)	−223.01	−227.61	−74.89
$MnCO_3$ (c)	−881.7	−811.4	109.5
$MnCl_2$ (c)	−481.2	−440.4	118.2
$MnCl_2 \cdot 4H_2O$ (c)	−1687	−1426	316.5
MnO (c)	−385.1	−363.3	61.5
MnO_2 (c)	−521.5	−466.7	53.1
Mn $(OH)_2$ (c)	−700.0	−618.7	94.9
Mn_3O_4 (hausmannite, c)	−1387.6	−1282.9	154.8
MnO_4^- (sln)	−542.66	−449.36	191.21
Mn_2O_7 (c)	−728.43	−543.92	—
$MnSO_4$ (c)	−1066.7	−959.0	112.5
Mo (g)	658.98	604.91	181.84
Mo (c)	0	0	28.6
$Mo(CO)_6$ (c)	−983.2	−878.6	327
$MoCl_2$ (c)	−288.7	−144.77	119.24

Continuation

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
$MoCl_3$ (c)	−393	−204	138
$MoCl_4$ (c)	−479.5	−391.6	180
$MoCl_5$ (c)	−526.8	−420.6	230
MoF_6 (c)	−1585.4	−1473.0	259.7
MoO_2 (c)	−589.1	−533.2	46.28
MoO_3 (c)	−745.2	−668.1	77.74
MoO_4^{2-} (sln)	−996.63	−915.46	58.58
H_2MoO_4 (c)	−1046.1	−950	159
MoS_2 (c)	−248.1	−239.2	62.59
N (g)	472.78	455.5	153.2
N_2 (g)	0	0	199.9
NF_3 (g)	—126	−84.4	260.6
NH_2OH (c)	−115	−17.4	66.5
NH_2OH (sln)	−98.3	−23.4	167.4
NH_3 (g)	−46.19	−16.71	192.6
NH_4^+ (sln)	−132.4	−79.5	114.4
$(NH_4)_2Al_2(SO_4)_4$ (c)	−5946.9	−4938.5	686.2
NH_4Br (c)	−270.1	−174.7	112.9
NH_4CNS (c)	−82.0	10.5	261.12
NH_4Cl (c)	−314.2	−203.2	95.8
NH_4ClO_4 (c)	−295.9	−88.8	184.3
NH_4NO_2 (sln)	−237.4	−116.8	253.7
NH_4NO_3 (c)	−365.4	−183.9	151.0
$(NH_4)_2SO_4$ (c)	−1180.0	−901.3	220
$(NH_4)_2CrO_4$ (c)	−1182.4	−995.8	167.78
$(NH_4)_2Cr_2O_7$ (c)	−1799.12	—	—
NH_4VO_3 (c)	−1051	−886.2	140.6
NO (g)	90.25	86.58	210.6
NOBr (g)	82.2	82.4	273.5
NOCl (g)	52.5	66.9	261.5
NOF (g)	−66.5	−51.0	247.9
NOI (g)	100	92.4	282.8
NO_2 (g)	33	51.5	240.2
NO_2Cl (g)	12.55	54.39	272.04
NO_2F (g)	−108.78	−66.45	260.15
NO_3^- (sln)	−207.5	−111.7	147.3
NO_3F (g)	10.46	73.61	292.83
N_2H_4 (g)	95.40	159.28	238.36
N_2H_4 (l)	50.50	149.2	121.4
N_2O (g)	82.1	104.2	220.0
N_2O_3 (g)	83.3	140.6	307.3
N_2O_4 (l)	19.05	98.0	209.3
N_2O_5 (c)	42.7	114.2	178.4
HN_3 (g)	294.00	328.03	238.86
HN_3 (l)	—	327.2	140.6
HNO_2 (sln)	−119.2	−55.6	152.7
HNO_3 (g)	−135.1	−74.8	266.9
HNO_3 (l)	−174.3	−80.3	156.6
Na (g)	108.3	77.3	153.6
Na (c)	0	0	51.45
Na (l)	2.48	10.5	57.9
Na^+ (g)	606.1	575.6	147.9
Na^+ (sln)	−239.9	−262.13	58.91

Continuation

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
$NaAlCl_4$ (c)	−1142.8	−1041.8	123.85
$NaAlH_4$ (c)	−114.5	−48.53	123.85
$NaAlO_2$ (c)	−1132.2	−1066.27	70.4
$NaAlSiO_4$ (nepheline, c)	−4051.5	−1960.7	124.26
$NaBH_4$ (c)	−183.3	−119.5	101.3
$NaBO_2$ (c)	−1059	−922.8	73.39
NaBr (c)	−361.4	−349.3	86.82
$NaBrO_3$ (c)	−342.8	−252.6	130.5
NaCN (c)	−89.8	−80.4	118.5
NaCNO (c)	−93.6	−81.4	124.85
NaCNS (c)	−410.0	−362.4	113
NaCl (g)	−189.4	−201.3	229.7
NaCl (c)	−411.1	−384.0	72.12
$NaClO_3$ (c)	−365.4	−275	129.7
$NaClO_4$ (c)	−382.8	−282	140
NaF (c)	−573.6	−543.3	51.3
NaF·HF (c)	−902.8	−806.74	90.7
NaH (c)	−56.4	−38	188
$NaHCO_3$ (c)	−947.7	−851.9	102
NaI (c)	−287.9	−284.6	98.5
$NaNO_2$ (c)	−359	−295	106
$NaNO_3$ (c)	−466.7	−365.9	116
NaN_3 (c)	21.3	99.9	70.5
NaOH (c)	−425.6	−380.7	64.4
NaOH (sln)	−470	−419.2	48.1
NaO_3 (c)	—	−217.6	115.9
$Na_2B_4O_7$ (c)	−3276.6	−3081.6	189.5
Na_2CO_3 (c)	−1131.0	−1047.5	136.4
$Na_2CO_3\cdot 10H_2O$ (c)	−4083.5	−3424.3	564.7
Na_2CrO_4 (c)	−1333	−1232	174.5
Na_2O (c)	−416	−376.1	72.4
Na_2O_2 (c)	−510.4	−446.9	94.88
Na_2S (c)	−370.3	−354.8	77.4
Na_2SO_3 (c)	−1090	−1002	146.0
Na_2SO_4 (c)	−1384.6	−1266.8	149.5
$Na_2SO_4\cdot 10H_2O$ (c)	−4324.17	−3642.9	591.9
$Na_2S_2O_3\cdot 5H_2O$ (c)	−2602.4	−1043	—
Na_2SiO_3 (c)	−1525.4	−1427.7	113.8
Na_3AlF_6 (c)	—	−3140.7	238.5
Na_3PO_4 (c)	−1935.5	−1819	224.7
Nb (g)	742.66	698.05	186.14
Nb (c)	0	0	36.6
$NbCl_5$ (c)	−797.5	−687.7	226
NbF_5 (c)	−1813.8	−1698.7	157.3
Nb_2O_5 (c)	−1898	−1764.1	137.2
Ne (g)	0	0	146.2
Ni (g)	423.67	378.29	182.1
Ni (c)	0	0	29.9
Ni^{2+} (sln)	−53.2	−45.59	−126.13
$NiBr_2$ (c)	−214	−201	129
$NiCl_2$ (c)	−304.2	−258.0	98.07
$NiCl_2\cdot 4H_2O$ (c)	—	−1250.6	—
NiF_2 (c)	−661.07	−624.25	73.6

Continuation

Substance	$\Delta H^\circ_{f,298}$, kJ/mol	$\Delta G^\circ_{f,298}$, kJ/mol	S°_{298}, J/(mol·deg)
NiI_2 (c)	−96.23	−89.12	157.74
$Ni(NH_3)_6^{2+}$ (sln)	—	−252.97	356.49
NiO (c)	−239.7	−211.6	37.99
$Ni(OH)_2$ (c)	−543.5	−458.3	80
$Ni(OH)_3$ (c)	−678.23	−541.83	81.59
NiS (c)	−79	−76.9	52.97
$NiSO_4$ (c)	−873.5	−763.8	103.85
$NiSO_4 \cdot 7H_2O$ (c)	−2977.4	−2463.3	378.9
O (g)	246.8	231.8	160.9
O_2 (g)	0	0	205.04
O_3 (g)	142.3	162.7	238.8
OH^- (sln)	−230.19	−157.42	−10.86
H_2O (g)	−241.82	−228.61	188.72
H_2O (l)	−285.83	−237.24	70.08
H_2O_2 (l)	−187.8	−120.4	109.5
Os (g)	669.44	621.78	191.63
Os (c)	0	0	32.6
OsO_4 (c)	−394.0	−302.5	164
P (g)	314.64	278.28	163.1
P (c, white)	0	0	41.1
P (c, black)	−38.9	−33.47	22.7
P (c, red)	−17.6	−11.9	22.8
P_4 (g)	58.9	24.5	279.9
PBr_3 (g)	−132.0	−155.7	348
PBr_3 (l)	−184	−175.7	240.2
PCl_3 (g)	−287.02	−260.5	311.7
PCl_5 (g)	−374.9	−305.4	364.5
PF_3 (g)	−956.5	−935.66	272.6
PF_5 (g)	−1593	−1517.2	296
PH_3 (g)	5.44	13.39	210.1
$POCl_3$ (l)	−597.1	−521.3	222.5
POF_3 (g)	−1197.3	−1148.95	284.9
P_4O_6 (c)	−1640	—	—
P_4O_{10} (c)	−2984.0	−2697.8	228.8
HPO_3 (c)	−976.9	—	—
HPO_4^{2-} (sln)	−1298.7	−1094.1	−36.8
$H_2PO_4^-$ (sln)	−1302.5	−1135.1	90.37
$H_2P_2O_7^{2-}$ (sln)	−2278.6	−2015.0	175.7
H_3PO_3 (sln)	−964.8	−856.8	167.3
H_3PO_4 (sln)	−1288.3	−1142.6	158.1
H_3PO_4 (c)	−1279	−1119.1	110.5
Pb (g)	195.6	162.2	175.3
Pb (c)	0	0	64.8
$PbCO_3$ (c)	−699.6	−625.9	131.0
$PbCl_2$ (c)	−359.8	−314.05	134.9
$PbCrO_4$ (c)	−910.9	−819.6	152.7
PbI_2 (c)	−175.2	−173.6	175.4
$Pb(NO_3)_2$ (c)	−451.7	−256.9	217.9
PbO (c)	−219.3	−189.1	66.2
PbO_2 (c)	−276.6	−218.3	74.89
Pb_3O_4 (c)	−723.4	−606.2	211.3
$Pb(OH)_2$ (c)	−512.5	−451.2	—
PbS (c)	−100.4	−98.8	91.2

Continuation

Substance	$\Delta H^\circ_{f,\ 298}$, kJ/mol	$\Delta G^\circ_{f,\ 298}$, kJ/mol	S°_{298}, J/(mol·deg)
$PbSO_4$ (c)	−920.6	−813.8	148.67
Pd (g)	393.3	354.81	166.94
Pd (c)	0	0	37.7
$PdCl_6^{2-}$ (sln)	−621.7	−440.9	231.03
PdO (c)	−115.5	−85.3	38.9
Pt (g)	564	519.14	192.3
Pt (c)	0	0	41.5
$PtBr_4$ (c)	−159	−105	163.5
$PtCl_4$ (c)	−229.3	−163.8	267.9
$PtCl_4^{2-}$ (sln)	−501.16	−363.0	155.03
$PtCl_6^{2-}$ (sln)	−669.9	−485.61	223.6
PtI_4 (c)	−59.4	−97.9	281
PtO_2 (c)	−134	−84	69.1
Rb (g)	81.9	54.0	169.9
Rb (c)	0	0	76.2
RbBr (c)	−389.2	−378.1	112.3
Rb_2CO_3 (c)	−1128.0	−1046.0	—
RbCl (c)	−430.6	−405.8	91.6
RbH (c)	54.31	−33.9	—
RbF (c)	−549.3	−523.4	75.3
RbI (c)	−328.4	−325.5	118
$RbNO_3$ (c)	−489.7	−390.4	140.6
RbOH (c)	−413.8	−364.0	79.5
Rb_2O (c)	−330.1	−292.9	108.8
Re (g)	776.76	731.55	187.82
Re (c)	0	0	36.5
$ReBr_3$ (c)	−164.43	−140.58	184.1
$ReCl_3$ (c)	−263.6	−199.99	158.99
$ReCl_5$ (c)	−361	−252.6	230
ReF_6 (l)	−1382.1	−1270.5	270.6
ReO_2 (c)	−423.84	−373.21	72.80
ReO_3 (c)	−592.9	−514.4	82.8
Re_2O_7 (c)	−1272	−1098	207.2
ReO_4^- (sln)	−791.61	−698.73	202.09
$HReO_4$ (c)	−761.49	−656.89	152.3
ReS_2 (c)	−138.9	−173.6	96.23
Re_2S_7 (c)	−451.4	−422.58	—
Rh (g)	556.89	510.91	—
Rh (c)	0	0	31.5
$RhCl_6^{3-}$ (sln)	—	−662.33	209.20
Ru (g)	602.5	555.63	186.4
Ru (c)	0	0	28.5
RuO_2 (c)	−236.4	−184.1	60.67
RuO_4 (c)	−239.3	−150.6	141.0
S (g)	273.0	232.4	167.7
S (c, monocl.)	0.38	0.188	32.6
S (c, rhomb.)	0	0	31.9
S^{2-} (sln)	35.81	92.47	−26.78
S_2 (g)	127.6	78.6	228.18
S_8 (g)	101.95	45.6	444.2
S_2Cl_2 (l)	−58.2	—	—
SO_2 (g)	−296.9	−300.2	248.1
SO_2 (c)	−331.1	—	—

Continuation

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
SO_2Cl_2 (l)	−391.2	−305.0	216.3
SO_3 (g)	−396.1	−370	256.4
SO_3 (l)	−439.0	−368.04	122.05
SO_3 (c)	−454.51	−368.98	52.3
H_2S (g)	−21	−33.8	205.7
H_2S (sln)	−39.75	−27.9	121.3
H_2SO_4 (l)	−814.2	−690.3	156.9
SO_4^{2-} (sln)	−910.85	−744.93	20.08
Sb (g)	268.57	228.46	180
Sb (c)	0	0	45.69
$SbCl_3$ (c)	−381.2	−322.5	110.5
Sb_2O_5 (c)	−1007.5	−864.7	125.1
Sc (g)	343.09	302.21	174.68
Sc (c)	0	0	34.3
Sc_2O_3 (c)	−1908.6	−1917.5	77
Se (c)	0	0	42.2
Se (vitr.)	5.9	2.65	51.5
SeF_6 (g)	—	−928.9	313.8
SeO_2 (c)	−225.7	−171.6	66.7
H_2Se (g)	33.4	19.7	219.0
Si (g)	468.61	407.6	167.9
Si (c)	0	0	18.8
SiC (c)	−66.8	−60.35	16.62
$SiCl_4$ (l)	−687.8	−598.3	239.7
SiF_4 (g)	−1614.9	−1572.5	282.6
SiF_6^{2-} (sln)	−2399	−2210.9	126.9
SiH_4 (g)	34.7	57.2	204.56
Si_2H_6 (g)	79.9	126.1	274.5
SiO_2 (quartz, c)	−908.3	−854.2	42.7
SiS_2 (l)	−156.1	−158.6	90.5
H_2SiO_3 (am.)	−1189.1	−1019.1	—
H_4SiO_4 (am.)	−1480	—	—
Sn (g)	302.1	267.3	168.4
Sn (c, white)	0	0	51.6
Sn (c, grey)	−2.1	−0.13	44.2
Sn^{2+} (sln)	−10.5	−27.3	−22.7
Sn^{4+} (sln)	−2.43	−2.4	−226.1
$SnCl_4$ (l)	−528.9	−457.7	299.6
SnH_4 (g)	162.3	187.8	228.7
SnO (c)	−286.0	−256.9	56.5
SnO_2 (c)	−580.8	−519.9	52.3
$Sn(OH)_2$ (c)	−506.3	−491.6	87.7
$Sn(OH)_4$ (c)	—	−946	155
SnS (c)	−110.2	−108.3	77.0
SnS_2 (c)	−82.5	−74.1	87.5
$SnSO_4$ (c)	−887	—	—
$Sn(SO_4)_2$ (c)	−1650	−1451.0	155.2
Sr (g)	164	130.9	135.1
Sr (c)	0	0	53.1
Sr^{2+} (sln)	−545.51	−557.3	−26.4
$SrCO_3$ (c)	−1218.4	−1137.6	97.1
$SrCl_2$ (c)	−828.4	−781.2	117
SrF_2 (c)	−1209.2	−1160.6	81.6

Continuation

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	$\Delta G^\circ_{f,\,298}$, kJ/mol	S°_{298}, J/(mol·deg)
SrI_2 (c)	−566.9	−559.8	159
$Sr(NO_3)_2$ (c)	−975.9	−778.2	195.5
SrO (c)	−590.4	−559.8	54.4
$Sr(OH)_2$ (c)	−959.4	−870.3	86.6
SrS (c)	−52.3	−447.7	68.2
$SrSO_4$ (c)	−1451.0	−1334.3	119.7
Ta (g)	781.99	739.2	185.1
Ta (c)	0	0	41.50
$TaCl_5$ (c)	−857.9	−750.5	238
TaF_5 (c)	−1903.6	−1790.8	170
Ta_2O_5 (c)	−2045.14	−1909.99	143.01
Tc (g)	648.52	604.55	180.96
Tc (c)	0	0	33.50
TcO_4^- (sln)	−723.8	−630.24	313.8
Tc_2O_7 (c)	−1114.6	−937.8	191.6
$HTcO_4$ (c)	−709.49	−591.07	139.33
Te (g)	191.7	152.0	182.4
Te (c)	0	0	49.56
TeF_6 (c)	−1323.0	−1226.4	337.26
TeO_2 (c)	−322.6	−270.2	798
Ti (g)	471.12	426.53	180.2
Ti (c, α)	0	0	30.6
$TiBr_4$ (c)	−619.2	−592	243.5
TiC (c)	−209	−205.7	24.7
$TiCl_2$ (c)	−516.7	−472.67	105.85
$TiCl_3$ (c)	−719.6	−653.96	139.12
$TiCl_4$ (g)	−763.2	−726.12	352.23
$TiCl_4$ (l)	−804.2	−737.4	252.4
TiF_4 (am.)	−1649.3	−1559.2	133.95
TiH_2 (c)	−144.35	−105.13	29.71
TiI_4 (g)	−287	−337.7	432.97
TiI_4 (c)	−386.6	−381.6	246
TiN (c)	−336.81	−308.1	30.1
TiO (c)	−526.3	−496.93	34.79
TiO_2 (c, rutile)	−943.9	−888.6	50.33
Ti_2O_3 (c)	−1518	−1431.0	77.3
H_2TiO_3 (c)	—	−1058.55	—
$Ti(OH)_3$ (c)	−1188.26	—	—
Tl (c)	0	0	64.18
TlBr (c)	−172.7	−167.4	122.6
Tl(OH) (c)	−233.5	−190.6	255.2
$Tl(OH)_3$ (c)	−516.6	—	102.1
Tl_2O (c)	−167.4	−153.1	161.1
Tl_2O_3 (c)	−390.4	−321.4	148.1
TlF (c)	−327	−306.2	95.69
TlCl (c)	−204.1	−185.0	111.5
$TlCl_3$ (c)	−311.3	−290.8	—
V (g)	515	468.6	182.2
V (c)	0	0	28.9
V^{2+} (sln)	−221.9	−218.1	−114.32
V^{3+} (sln)	−257.9	−242.8	−217.53
VCl_2 (c)	−452.17	−406.12	97.1
VCl_3 (c)	−582.41	−516.52	130.96

Continuation

Substance	$\Delta H^\circ_{f,\ 298}$, kJ/mol	$\Delta G^\circ_{f,\ 298}$, kJ/mol	S°_{298}, J/(mol·deg)
VCl_4 (l)	−569.8	−505.6	259
VF_2 (c)	−837.4	−791.3	77.5
VF_5 (l)	−1480.9	−1378.4	191.9
VN (c)	−217.15	−191.21	37.28
VO (c)	−431.8	−402.6	33.6
VO^{2+} (sln)	—	−456.06	−108.78
VO_2 (c)	−720	−665	51.57
V_2O_3 (c)	−1219.1	−1139.4	98.3
V_2O_5 (c)	−1552	−1421.2	131
W (g)	844.33	802.26	173.85
W (c)	0	0	32.7
WC (c)	−41.0	−39.5	35
W $(CO)_6$ (g)	−876.96	−825.9	4.184
WO_2Cl_2 (c)	−835.54	−753.8	186.61
WF_6 (g)	−1721.5	−1635.9	353.5
WO_2 (c)	−589.63	−533.87	50.55
WO_3 (c)	−842.7	−763.9	75.94
WO_4^{2-} (sln)	−1115.45	−920.48	62.76
H_2WO_4 (c)	−1132	−1036.4	117.2
Y (g)	426.77	384.9	—
Y (c)	0	0	46.0
YCl_3 (c)	−982.4	−900	136.8
Y_2O_3 (c)	−1904	−1800	99.2
$Y(OH)_3$ (c)	−1412.5	−1290.0	96.3
Zn (g)	130.73	95.19	160.87
Zn (c)	0	0	41.63
Zn^{2+} (sln)	−153.74	−147.26	−110.67
$ZnBr_2$ (c)	−329.7	−312.4	136
$ZnCO_3$ (c)	−810.74	−732.48	92.47
$ZnCl_2$ (c)	−415.05	−369.4	111.5
ZnF_2 (c)	−764.4	−713.5	73.68
ZnI_2 (c)	−208.2	−209.3	161.5
$Zn(NH_3)_4^{2+}$ (sln)	−67.7	−53.64	—
$Zn(NO_3)_2$ (c)	−514.63	−298.82	193.72
$Zn(NO_3)_2 \cdot 2H_2O$ (c)	−1111.05	−795.9	258.21
$Zn(NO_3)_2 \cdot 6H_2O$ (c)	−2306.8	−1174.9	462.3
ZnO (c)	−350.6	−320.7	43.64
$Zn(OH)_2$ (c)	−645.4	−555.9	76.99
$Zn(OH)_4^{2-}$ (sln)	—	−905.42	—
ZnS (c)	−205.4	−200.7	57.74
$ZnSO_4 \cdot 6H_2O$ (c)	−2780.83	−2325.56	363.8
$ZnSO_4 \cdot 7H_2O$ (c)	−3078.5	−2563.9	388.7
Zr (g)	608.42	565.97	187.24
Zr (c)	0	0	39.0
ZrC (c)	−206.7	−197.4	33.3
$ZrCl_4$ (c)	−979.8	−889.3	181.4
ZrF_4 (c)	−1911.3	−1809.9	104.6
ZrO_2 (c)	−1100.6	−1042.8	50.38
$ZrOCl_2$ (c)	−986.6	−992.4	—
$ZrOCl_2 \cdot 8H_2O$ (c)	−3468	−2986.96	—

Appendix 16

Heat of Ion Hydration in Solutions of Infinite Dilution at 25° C

Heat of hydration is the amount of heat which is liberated during transition of 1 mole of ion from vacuum to aqueous solution.

Ion	ΔH, kJ/mol	Ion	ΔH, kJ/mol	Ion	ΔH, kJ/mol
Ag^+	−489.53	Fe^{2+}	−1924.6	OH^-	−510.45
Al^{3+}	−4694.5	Fe^{3+}	−4485.3	Os^{2+}	−1857.7
Au^+	−644.3	Ga^{3+}	−4702.8	Pb^{2+}	−1514.6
Ba^{2+}	−1338.83	H^+	−1108.76	Pd^{2+}	−2112.9
Br^-	−317.98	Hg^{2+}	−1845.14	Pt^{2+}	−2188.2
CN^-	−347.27	I^-	−280.33	Rb^+	−313.80
CO_3^{2-}	−1389.09	In^{3+}	−4163	Ru^{2+}	−1874
Ca^{2+}	−1615.02	Ir^{2+}	−1996	Sc^{3+}	−3962
Cd^{2+}	−1836.72	K^+	−338.90	Sn^{2+}	−1565
Cl^-	−351.46	Li^+	−531.36	Sn^{4+}	−7644
CNS^-	−309.62	Mg^{2+}	−1953.94	SO_4^{2-}	−1108.76
Co^{2+}	−2079.4	Mn^{2+}	−1878.6	Sr^{2+}	−1476.95
Co^{3+}	−4711.2	Mn^{3+}	−4594	Ti^{2+}	−1822
ClO_4^-	−225.94	NH_4^+	−326.35	Ti^{3+}	−4297
Cr^{2+}	−1924.6	NO_3^-	−309.62	Tl^+	−343.09
Cr^{3+}	−4623	Na^+	−422.59	Tl^{3+}	−4117
Cs^+	−280.33	Ni^{2+}	−2138.02	V^{2+}	−1895
Cu^+	−581.6	OH_3^+	−460.24	V^{3+}	−4406
Cu^{2+}	−2129.7			Zn^{2+}	−2075.26
F^-	−485.34				

Appendix 17

Thermodynamic Parameters of Phase Conversions of Simple Substances*

Simple substance	T_{melt}, K	ΔH_{melt}, kJ/mol	ΔS_{melt}, J/deg·mol	T_{boil}, K	ΔH_{evap}, kJ/mol, at T_{boil}	ΔS_{evap}, J/deg·mol, at T_{boil}
Ag	1234	11.304	9.1	2450	255.23	104.7
Al	932	10.676	11.47	2720	293.9	108.0
Ar	83.78	1.1752	14.07	87.27	6.523	74.9
As	1096	27.7	25.46	(1500)	67.95	35.63
Au	1336	12.372	11.93	2980	324.64	106.8
B	2300	22.2	9.76	4200	539.3	112.2
Ba	983	7.6	7.78	1910	651.0	79.21
Be	1556	11.7	7.5	2750	295	107.0
Bi	544.5	11.14	19.97	1832	151.6	82.71
Br_2	265.95	10.80	20.1	331.95	29.94	90.4
C (graphite)	4100	(126)	(29.3)	(5700)	(586)	(105)
Ca	1123	8.667	7.04	1765	150.05	85.0
Cd	594	6.071	9.80	1038	99.94	96.7

Simple substance	T_{melt}, K	ΔH_{melt}, kJ/mol	ΔS_{melt}, J/deg·mol	T_{boil}, K	ΔH_{evap}, kJ/mol, at T_{boil}	ΔS_{evap}, J/deg·mol, at T_{boil}
Cl_2	172.17	5.61	16.3	239.55	19.80	83.3
Co	1765	15.36	8.71	3150	382.7	121.4
Cr	2176	13.8	6.36	2915	349.01	121.0
Cs	301.8	2.14	7.08	958	65.942	68.75
Cu	1356	13.063	9.6	2855	304.80	106.8
F_2	53.69	0.51	4.77	85.17	6.54	77.0
Fe	1809	13.56	7.49	3160	351.3	111
Ga	302.8	3.27	6.74	2320	226.5	97.6
Gd	1585	10.05	6.36	(3000)	(311.9)	(103.8)
Ge	1210.4	31.8	26.29	3100	334.55	107.6
He	—	—	—	4.215	81.2×10^{-3}	19.3
Hf	2493	(21.8)	(8.8)	(5500)	(661)	120.2
Hg	234.29	2.297	9.76	629.88	59.19	94.2
I_2	386.65	16.16	23.0	457.65	41.9	91.3
In	429.32	3.27	6.74	2320	226.5	97.6
Ir	2727	(26.4)	(9.59)	4400	564	128.1
K	336.4	2.32	6.90	1039	77.581	68.87
Kr	116.45	1.6358	14.07	119.80	9.035	74.5
La	1193	6.201	5.19	3640	399.8	109.7
Li	453.70	3.026	6.65	1604	134.77	83.7
Mg	923	8.960	9.71	1390	128.74	92.44
Mn	1517	(14.6)	(9.67)	2314	219.89	95.4
Mo	2890	27.63	9.54	5100	594	131.5
Na	370.97	2.603	6.72	1163	89.095	77.25
Nb	2740	(26.8)	(9.6)	5200	692.9	134.0
Ni	1728	17.63	10.22	3110	372.08	119.8
Os	3045	(31.8)	(10.5)	(4500)	(628)	(138)
P (cubic)	317.3	0.63	1.97	548.1	14.07	25.5
Pb	600.6	4.777	7.87	2024	179.5	86.7
Pd	1825	16.50	9.04	3400	394	119.3
Po	519	(5.0)	(9.6)	1235	(60.29)	48.86
Pt	2042	22.2	10.9	4100	511	124.8
Ra	973	(14.2)	(7)	(1800)	—	—
Rb	312.0	2.20	7.40	974	69.250	71.17
Re	3453	(33.1)	(9.6)	5900	707	120.2
Rh	2233	(20.5)	(9.2)	(4000)	(494)	(123.9)
Ru	2583	(27.2)	(10.5)	(4000)	(569)	(142)
$S_{rhomb.}$	385.95	1.591	4.10	717.7	9.21	12.85
Sb	903	19.85	21.98	1910	67.95	35.63
Se	490	5.44	11.14	958	26.33	27.51
Si	1683	46.5	27.6	(4000)	(419)	(105)
Sn	505	7.20	14.24	2960	290.6	98.0
Sr	1043	(9.21)	7.92	1640	139.00	84.57
Ta	3250	(31.8)	(9.6)	5700	754	132.3
Tc	2413	(23.0)	(9.61)	(4900)	578	(117.0)
Te	723	17.50	24.2	1263	50.7	40.24
Ti	1940	15.83	8.15	3550	429.1	121.0
Tl	577	4.27	4.27	1740	162.2	92.0
U	1406	8.524	6.07	4200	423	100.9
V	2193	16.96	7.74	3650	458.9	125.6
W	3650	34.5	9.6	5800	800.0	137.7

Continuatión

Simple substance	T_{melt}, K	ΔH_{melt}, kJ/mol	ΔS_{melt}, J/deg·mol	T_{boil}, K	ΔH_{evap}, kJ/mol, at T_{boil}	ΔS_{evap}, J/deg·mol, at T_{boil}
Xe	161.25	2.2965	14.24	165.06	12.644	77.0
Zn	692.7	7.400	10.68	1181	115.39	97.6
Zr	2125	(16.7)	7.8	4650	582	125.2

* Hypothetic values are given in parentheses. The values of ΔH_{evap} and S_{evap} (except for halogens) are given without consideration of atom association in the liquid phase or vapour.

Appendix 18

Energy of Crystal Lattice (kJ/mol)

Ion	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	OH^-
Li^+	1024	841.8	802.0	748.0	2900	—	854.0
Na^+	940.0	774.0	741.0	694.0	—	—	884.5
K^+	830.0	730.0	677.5	637.5	—	—	790.5
Rb^+	774.0	678.0	654.0	618.0	—	—	766.0
Cs^+	732.0	646.0	625.5	592.0	—	—	720.0
NH_4^+	816.0	640.0	615.0	578.0	—	—	—
Ag^+	942	892.0	876	866	2455	—	—
Cu^+	—	866.0	829.0	787.0	2720	2580	—
Mg^{2+}	2885	2480	2424	2530	3810	3260	—
Ca^{2+}	2580	2198	2128	2040	3520	3020	—
Sr^{2+}	2430	2110	—	1954	3320	2875	—
Ba^{2+}	2290	1958	1938	1840	3127	2248	—
Cu^{2+}	—	2762	—	—	4130	3725	—
Zn^{2+}	—	2690	2650	2595	4060	3565	—
Cd^{2+}	2770	2502	2480	2358	3820	3358	—

Overall Stability Constants of Complex Ions

$$M + nL = ML_n, \quad K_{st} = \frac{[ML_n]}{[M]\,[L]^n}$$

Complex ion	K_{st}	log K_{st}	Complex ion	K_{st}	log K_{st}
Ammonia			**Ethylenediamine**		
$Ag(NH_3)_2^+$	1.47×10^{7}	7.24	$Co(en)_3^{3-}$	4.9×10^{48}	48.69
$Cd(NH_3)_4^{2+}$	3.63×10^{6}	6.56	$Cu(en)_2^{2+}$	1.35×10^{20}	20.13
$Co(NH_3)_6^{2+}$	2.45×10^{4}	4.39	$Ni(en)_3^{2+}$	1.29×10^{19}	19.11
$Co(NH_3)_6^{3+}$	1.99×10^{35}	35.3	**Fluoride**		
$Cu(NH_3)_2^{2+}$	7.25×10^{10}	10.86			
$Cu(NH_3)_4^{2+}$	1.07×10^{12}	12.03	AlF_6^{3-}	4.68×10^{20}	20.67
$Hg(NH_3)_4^{2+}$	1.99×10^{19}	19.3	FeF_6^{3-}	1.26×10^{16}	16.10
$Ni(NH_3)_6^{2+}$	1.02×10^{8}	8.01	**Hydroxy**		
$Zn(NH_3)_4^{2+}$	5.01×10^{8}	8.7			
			$Ag(OH)_2^-$	1.00×10^{4}	4.0
Bromide			$Al(OH)_4^-$	1.00×10^{33}	33.0
$AgBr_2^-$	2.19×10^{7}	7.34			
$AuBr_2^-$	2.88×10^{12}	12.46	$Cd(OH)_4^{2-}$	2.63×10^{8}	8.42
$BiBr_4^-$	6.92×10^{7}	7.84	$Cr(OH)_4^-$	7.94×10^{29}	29.9
$CdBr_4^{2-}$	5.01×10^{3}	3.7	$Cu(OH)_4^{2-}$	3.63×10^{14}	14.56
$HgBr_4^{2-}$	1.00×10^{21}	21.00	$Fe(OH)_4^{2-}$	3.63×10^{8}	8.56
$ZnBr_4^{2-}$	3.16×10^{-3}	−2.5	$Zn(OH)_4^{2-}$	5.02×10^{17}	17.70
Chloride			**Iodide**		
$AgCl_2^-$	1.1×10^{5}	5.04			
$AuCl_2^-$	2.63×10^{9}	9.42	AgI_2^-	5.5×10^{11}	11.74
$AuCl_4^-$	2.0×10^{21}	21.30	BiI_4^-	8.91×10^{14}	14.95
$BiCl_6^{3-}$	2.63×10^{6}	6.42	CdI_4^{2-}	2.24×10^{5}	5.35
$CdCl_4^{2-}$	5.01×10	1.7	HgI_4^{2-}	6.76×10^{29}	29.83
$CuCl_2^-$	2.24×10^{5}	5.35	PbI_4^{2-}	8.32×10^{3}	3.92
$HgCl_4^{2-}$	1.66×10^{15}	15.22	ZnI_4^{2-}	3.1×10^{-1}	−0.512
$SnCl_4^{2-}$	30.2	1.48	**Nitrite**		
$SnCl_6^{2-}$	6.61×10^{6}	6.82			
$ZnCl_4^{2-}$	10^{-1}	−1.0	$Ag(NO_2)_2^-$	6.76×10^{2}	2.83
Cyanide			**Thiocyanate**		
$Ag(CN)_2^-$	7.08×10^{19}	19.85	$Ag(CNS)_2^-$	1.7×10^{8}	8.23
$Au(CN)_2^-$	2.0×10^{38}	38.3	$Co(CNS)_4^{2-}$	5.12×10^{-1}	−0.309
$Au(CN)_4^-$	10^{56}	56	$Fe(CNS)_6^{3-}$	1.70×10^{3}	3.23
$Cd(CN)_4^{2-}$	1.29×10^{17}	17.11	$Fe(CNS)_4^-$	3.39×10^{4}	4.53
$Co(CN)_6^{4-}$	1.23×10^{19}	19.09	$Hg(CNS)_4^{2-}$	1.7×10^{21}	21.23
$Cu(CN)_2^-$	1.00×10^{24}	24	**Thiosulphate**		
$Fe(CN)_6^{4-}$	7.94×10^{36}	36.9			
$Fe(CN)_6^{3-}$	7.94×10^{43}	43.9	$Ag(S_2O_3)_2^{3-}$	2.88×10^{13}	13.46
$Hg(CN)_4^{2-}$	9.33×10^{38}	38.97	$Cu(S_2O_3)_2^{3-}$	1.86×10^{12}	12.27
$Ni(CN)_4^{2-}$	1.0×10^{31}	31.0			

Acid Ionization Constants

$$HAn + H_2O \rightleftarrows H_3O^+ + An^-$$

$$K_a = \frac{[H_3O^+]\,[An^-]}{[HAn]}$$

Acid	Formula	K_a	$pK = -\log K_a$
Acetic	CH_3COOH	1.75×10^{-5}	4.75
Arsenic	H_3AsO_4		
K_1		6.46×10^{-3}	2.19
K_2		1.15×10^{-7}	6.94
K_3		3.16×10^{-12}	11.50
Boric	H_3BO_3	5.75×10^{-10}	9.24
Carbonic	H_2CO_3		
K_1		1.31×10^{-4}	3.88
K_2		5.0×10^{-11}	10.30
Chromic	H_2CrO_4		
K_1		2.1×10^{-1}	0.67
K_2		3.2×10^{-7}	6.50
Hydrobromic	HBr	1×10^{9}	−9.1
Hydrochloric	HCl	1×10^{7}	−7.1
Hydrocyanic	HCN	6.5×10^{-10}	9.19
Hydrofluoric	HF	6.6×10^{-4}	3.1
Hydrogen peroxide	H_2O_2	2.6×10^{-12}	11.58
Hydroiodic	HI	1.6×10^{11}	−10.7
Hydrosulphuric	H_2S		
K_1		1.0×10^{-7}	7.00
K_2		1.3×10^{-13}	12.89
Hypochlorous	HClO	3.2×10^{-8}	7.50
Hypophosphorous	H_3PO_2	7.9×10^{-2}	1.12
Iodic	HIO_3	1.7×10^{-1}	0.77
Nitric	HNO_3	4.36×10	−1.64
Nitrous	HNO_2	4×10^{-4}	3.4
Perchloric	$HClO_4$	—	~ −10
Periodic	H_5IO_6		
K_1		3.09×10^{-2}	1.57
K_2		7.08×10^{-9}	8.15
K_3		2.5×10^{-13}	12.6
Permanganic	$HMnO_4$	2×10^{2}	−2.3
Phosphoric	H_3PO_4		
K_1		7.25×10^{-3}	2.12
K_2		6.31×10^{-8}	7.20
K_3		1.26×10^{-12}	11.9
Phosphorous	H_3PO_3		
K_1		2.5×10^{-2}	1.6
K_2		2.0×10^{-1}	6.7
Silicic	H_4SiO_4		
K_1		2×10^{-10}	9.7
K_2		2×10^{-12}	11.7
K_3		1×10^{-12}	12
Sulphuric	H_2SO_4		
K_1		1×10^{3}	−3.0
K_2		1.2×10^{-2}	1.9

Continuation

Acid	Formula	K_a	$pK = -\log K_a$
Sulphurous	H_2SO_3		
K_1		1.3×10^{-2}	1.87
K_2		6.8×10^{-8}	7.27
Telluric	H_6TeO_6		
K_1		2.0×10^{-8}	7.70
K_2		1.0×10^{-10}	10.99
Thiocyanic	HSCN	1.4×10^{-1}	0.85

Appendix 21

Solubility Products of Sparingly Soluble Substances

Substance	sp	$p^{sp} = -\log sp$
AgBr	5.3×10^{-13}	12.28
AgCN	1.4×10^{-16}	15.84
AgCl	1.78×10^{-10}	9.75
Ag_2CrO_4	1.1×10^{-12}	11.95
$Ag_2Cr_2O_7$	1×10^{-10}	10
AgI	8.3×10^{-17}	16.08
Ag_3PO_4	1.3×10^{-20}	19.89
Ag_2S	6.3×10^{-50}	49.20
AgSCN	1.1×10^{-12}	11.97
$Al(OH)_3$ (Al^{3+}, $3OH^-$)	1×10^{-32}	32.0
$AlPO_4$	5.75×10^{-19}	18.24
AuBr	5.0×10^{-17}	16.3
$AuBr_3$	4.0×10^{-36}	35.4
AuCl	2.0×10^{-13}	12.7
$AuCl_3$	3.2×10^{-25}	24.5
AuI	1.6×10^{-23}	22.8
AuI_3	1×10^{-46}	46
$BaCO_3$	5.1×10^{-9}	8.29
$BaCrO_4$	1.2×10^{-10}	9.93
BaF_2	1.1×10^{-6}	5.98
$BaMnO_4$	2.5×10^{-10}	9.60
$Ba_3(PO_4)_2$	6.03×10^{-39}	38.22
$Ba_2P_2O_7$	3×10^{-11}	10.5
$BaSO_3$	8.0×10^{-7}	6.1
$BaSO_4$	1.1×10^{-10}	9.97
BaS_2O_3	1.6×10^{-5}	4.79
$Be(OH)_2$ (Be^{2+}, $2OH^-$)	6.3×10^{-22}	21.3
BiI_3	8.1×10^{-19}	18.09
Bi_2S_3	1×10^{-72}	72
$CaCO_3$	4.8×10^{-9}	8.32
$CaCrO_4$	7.1×10^{-4}	3.15
CaF_2	4.0×10^{-11}	10.40
$Ca_3(PO_4)_2$	2.0×10^{-29}	28.70
$CaSO_3$	1.3×10^{-8}	7.89
$CaSO_4$	9.1×10^{-6}	5.04

Continuation

Substance	sp	$p^{sp}=-\log sp$
$Cd(CN)_2$	1.0×10^{-8}	8.0
$Cd(OH)_2$ (freshly preciptd.)	2.2×10^{-14}	13.66
$Cd(OH)_2$ (aged)	5.9×10^{-15}	14.23
CdS	7.9×10^{-27}	26.10
CoS (α)	4.0×10^{-21}	20.40
CoS (β)	2.0×10^{-25}	24.76
CuBr	5.25×10^{-9}	8.28
CuCN	3.2×10^{-20}	19.49
CuCl	1.2×10^{-6}	5.92
CuI	1.1×10^{-12}	11.96
$Cu(OH)_2$	2.2×10^{-20}	19.66
$(CuOH)_2CO_3$	1.7×10^{-34}	33.78
CuS	6.3×10^{-36}	35.20
Cu_2S	2.5×10^{-48}	47.60
CuSCN	4.8×10^{-15}	14.32
$Fe(OH)_2$	1×10^{-15}	15.0
$Fe(OH)_3$	3.2×10^{-38}	37.50
FeS	5×10^{-18}	17.3
GeS	3×10^{-35}	34.5
HgI_2	$\sim 10^{-26}$	~ 26
HgS (black)	1.6×10^{-52}	51.8
HgS (red)	4.0×10^{-53}	52.40
In_2S_3	5.75×10^{-74}	73.24
$K_3[AlF_6]$	1.6×10^{-9}	8.80
KBF_4	2×10^{-3}	2.7
KBH_4	1.3×10^{-3}	2.7
$KClO_4$	1.1×10^{-2}	1.97
$K_3[Co(NO_2)_6]$	4.3×10^{-10}	9.37
Li_2CO_3	3.98×10^{-3}	2.40
$MgCO_3$	2.1×10^{-5}	4.67
MgF_2	6.5×10^{-9}	8.19
$Mg(OH)_2$	6.0×10^{-13}	12.6
$Mg_3(PO_4)_2$	1×10^{-13}	13
$Mn(OH)_2$	1.9×10^{-13}	12.72
MnS (flesh coloured)	2.5×10^{-10}	9.60
MnS (green)	2.5×10^{-13}	12.60
$(NH_4)_3AlF_6$	1.6×10^{-3}	2.80
$(NH_4)_2IrCl_6$	3×10^{-5}	4.5
Na_3AlF_6	4.1×10^{-10}	9.39
$Ni(CN)_2$	3×10^{-28}	22.5
$Ni(OH)_2$	2.0×10^{-15}	14.70
NiS	1×10^{-24}	24.0
$PbCO_3$	7.49×10^{-14}	13.13
$PbCl_2$	1.6×10^{-5}	4.79
$PbCrO_4$	1.8×10^{-14}	13.75
PbF_2	2.7×10^{-8}	7.57
PbI_2	1.1×10^{-9}	8.98
$Pb(OH)_2$	7.9×10^{-16}	15.1
PbS	2.5×10^{-27}	26.60
$PbSO_4$	1.6×10^{-8}	7.80
$PtBr_4$	3×10^{-41}	40.5
$PtCl_4$	8.0×10^{-29}	28.1

Continuation

Substance	sp	$p^{sp}=-\log sp$
PtS	8×10^{-73}	72.1
Sb_2S_3	1.6×10^{-93}	92.8
$Sn(OH)_2$	6.3×10^{-27}	26.20
SnS	1×10^{-25}	25.0
$SrCO_3$	1.1×10^{-10}	9.96
$SrCrO_4$	3.6×10^{-5}	4.44
SrF_2	2.5×10^{-9}	8.61
TlBr	3.89×10^{-6}	5.41
TlCl	1.7×10^{-4}	3.76
$Tl_3[Co(NO_2)_6]$	1.0×10^{-16}	16.00
TlI	6.5×10^{-8}	7.19
Tl_2S	5.0×10^{-21}	20.30
Tl_2SO_4	4×10^{-3}	2.4
$Zn(CN)_2$	2.6×10^{-13}	12.59
$Zn(OH)_2$	7.1×10^{-18}	17.15
α-ZnS (sphalerite)	1.6×10^{-24}	23.80
β-ZnS (wurtzite)	2.5×10^{-22}	21.60

Appendix 22

Standard Electrode Potentials of Selected Systems in Aqueous Solution

Equation	E°, V
Aluminium	
$AlO_2^- + 2H_2O + 3e^- = Al + 4OH^-$	-2.35
$AlF_6^{3-} + 3e^- = Al + 6F^-$	-2.07
$Al^{3+} + 3e^- = Al$	-1.663
Antimony	
$SbO_2^- + 2H_2O + 3e^- = Sb + 4OH^-$	-0.675
$SbO^+ + 2H^+ + 3e^- = Sb + H_2O$	0.212
$SbO_2^- + 4H^+ + 3e^- = Sb + 2H_2O$	0.446
$Sb_2O_5 + 6H^+ + 4e^- = 2SbO^+ + 3H_2O$	0.58
Arsenic	
$H_3AsO_4 + 2H^+ + 2e^- = HAsO_2 + 2H_2O$	0.56
$AsO_4^{3-} + 2H_2O + 2e^- = AsO_2^- + 4OH^-$	-0.71
Barium	
$Ba^{2+} + 2e^- = Ba$	-2.905
Beryllium	
$Be^{2+} + 2e^- = Be$	-1.847
$BeO_2^{2-} + 4H^+ + 2e^- = Be + 2H_2O$	-0.909

Equation	E°, V
Bismuth	
$Bi(OH)_3 + 3e^- = Bi + 3OH^-$	−0.46
$BiO^+ + 2H^+ + 3e^- = Bi + H_2O$	0.320
$NaBiO_3 + 4H + 2e^- = BiO^+ + Na^+ + 2H_2O$	1.8
Boron	
$BF_4^- + 3e^- = B + 4F^-$	−1.04
$BO_3^{3-} + 6H^+ + 3e^- = B + 3H_2O$	−0.165
Bromine	
$BrO^- + H_2O + 2e^- = Br^- + 2OH^-$	0.76
$Br_2 + 2e^- = 2Br^-$	1.065
$BrO_3^- + 6H^+ + 6e^- = Br^- + 3H_2O$	1.44
$2BrO_3^- + 12H^+ + 10e^- = Br_2 + 6H_2O$	1.52
$BrO_4^- + 2H^+ + 2e^- = BrO_3^- + H_2O$	1.88
Cadmium	
$CdS + 2e^- = Cd + S^{2-}$	−1.175
$Cd(CN)_4^{2-} + 2e^- = Cd + 4CN^-$	−1.09
$Cd(NH_3)_4^{2+} + 2e^- = Cd + 4NH_3$	−0.61
$Cd^{2+} + 2e^- = Cd$	−0.403
Calcium	
$Ca(OH)_2 + 2e^- = Ca + 2OH^-$	−3.03
$Ca^{2+} + 2e^- = Ca$	−2.866
Carbon	
$CO_2 + 2H^+ + 2e^- = CO + H_2O$	−0.12
$CO_3^{2-} + 6H^+ + 4e^- = C + 3H_2O$	0.475
Cesium	
$Cs^+ + e^- = Cs$	−2.923
Chlorine	
$2ClO^- + 2H_2O + 2e^- = Cl_2 + 4OH^-$	0.40
$ClO_4^- + 4H_2O + 8e^- = Cl^- + 8OH^-$	0.56
$ClO_3^- + 3H_2O + 6e^- = Cl^- + 6OH^-$	0.63
$ClO^- + H_2O + 2e^- = Cl^- + 2OH^-$	0.88
$ClO_4^- + H^+ + 2e^- = ClO_3^- + H_2O$	1.189
$Cl_2 + 2e^- = 2Cl^-$	1.359
$ClO_4^- + 8H^+ + 8e^- = Cl^- + 4H_2O$	1.38
$ClO_3^- + 6H^+ + 6e^- = Cl^- + 3H_2O$	1.451
Chromium	
$Cr^{2+} + 2e^- = Cr$	−0.913
$Cr^{3+} + 3e^- = Cr$	−0.744
$Cr^{3+} + e^- = Cr^{2+}$	−0.407
$CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3 + 5OH^-$	−0.13
$CrO_4^{2-} + 4H^+ + 3e^- = CrO_2^- + 2H_2O$	0.945
$CrO_2^- + 4H^+ + e^- = Cr^{2+} + 2H_2O$	1.188
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.333
$CrO_4^{2-} + 8H^+ + 3e^- = Cr^{3+} + 4H_2O$	1.477

Equation	E°, V
Cobalt	
$Co(CN)_6^{3-} + e^- = Co(CN)_6^{4-}$	−0.83
$Co^{2+} + 2e^- = Co$	−0.277
$Co(NH_3)_6^{3+} + e^- = Co(NH_3)_6^{2+}$	0.1
$Co(OH)_3 + e^- = Co(OH)_2 + OH^-$	0.17
$Co^{3+} + 3e^- = Co$	0.33
$Co^{3+} + e^- = Co^{2+}$	1.808
Copper	
$CuS + 2e^- = Cu + S^{2-}$	−0.71
$Cu(CN)_2^- + e^- = Cu + 2CN^-$	−0.43
$CuI + e^- = Cu + I^-$	−0.185
$Cu(NH_3)_4^{2+} + 2e^- = Cu + 4NH_3$	−0.07
$Cu^{2+} + e^- = Cu^+$	0.153
$Cu^{2+} + 2e^- = Cu$	0.337
$Cu^+ + e^- = Cu$	0.52
$Cu^{2+} + Cl^- + e^- = CuCl$	0.53
$Cu^{2+} + Br^- + e^- = CuBr$	0.64
$Cu^{2+} + I^- + e^- = CuI$	0.84
$Cu^{2+} + 2CN^- + e^- = Cu(CN)_2^-$	1.12
Fluorine	
$OF_2 + 2H^+ + 4e^- = 2F^- + H_2O$	2.1
$F_2 + 2e^- = 2F^-$	2.87
Gallium	
$Ga^{3+} + 3e^- = Ga$	−0.53
Germanium	
$H_2GeO_3 + 4H^+ + 2e^- = Ge^{2+} + 3H_2O$	−0.363
$H_2GeO_3 + 4H^+ + 4e^- = Ge + 3H_2O$	−0.13
$Ge^{2+} + 2e^- = Ge$	0.000
Gold	
$Au(CN)_2^- + e^- = Au + 2CN^-$	−0.61
$Au^{3+} + 2e^- = Au^+$	1.401
$Au^{3+} + 3e^- = Au$	1.498
$Au^+ + e^- = Au$	1.692
Hafnium	
$Hf^{4+} + 4e^- = Hf$	−1.70
Hydrogen	
$H_2 + 2e^- = 2H^-$	−2.251
$2H_2O + 2e^- = H_2 + 2OH^-$	−0.828
$2H^+ + 2e^- = H_2$	0.000
Iodine	
$2IO_3^- + 6H_2O + 10e^- = I_2 + 12OH^-$	0.21
$IO_3^- + 3H_2O + 6e^- = I^- + 6OH^-$	0.25
$2IO^- + 2H_2O + 2e^- = I_2 + 4OH^-$	0.45
$IO^- + H_2O + 2e^- = I^- + 2OH^-$	0.49
$I_2 + 2e^- = 2I^-$	0.536

Equation	E°, V
Iodine	
$2IO_3^- + 12H^+ + 10e^- = I_2 + 6H_2O$	1.19
$2HIO + 2H^+ + 2e^- = I_2 + 2H_2O$	1.45
$H_5IO_6 + H^+ + 2e^- = IO_3^- + 3H_2O$	1.60
$IO_4^- + 2H^+ + 2e^- = IO_3^- + H_2O$	1.64
Iridium	
$IrO_2 + 4H^+ + 4e^- = Ir + 2H_2O$	0.93
$Ir^{3+} + 3e^- = Ir$	0.15
Iron	
$FeS + 2e^- = Fe + S^{2-}$	−0.95
$FeCO_3 + 2e^- = Fe + CO_3^{2-}$	−0.756
$Fe(OH)_3 + e^- = Fe(OH)_2 + OH^-$	−0.53
$Fe^{2+} + 2e^- = Fe$	−0.440
$Fe^{3+} + 3e^- = Fe$	−0.037
$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-}$	0.356
$Fe^{3+} + e^- = Fe^{2+}$	0.771
$FeO_4^{2-} + 8H^+ + 3e^- = Fe^{3+} + 4H_2O$	1.700
Lead	
$Pb^{2+} + 2e^- = Pb$	−0.126
$PbO_3^{2-} + H_2O + 2e^- = PbO_2^{2-} + 2OH^-$	0.2
$PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 2H_2O$	1.449
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- = PbSO_4 + 2H_2O$	1.685
$Pb^{4+} + 2e^- = Pb^{2+}$	1.694
Lithium	
$Li^+ + e^- = Li$	−3.045
Magnesium	
$Mg(OH)_2 + 2e^- = Mg + 2OH^-$	−2.69
$Mg^{2+} + 2e^- = Mg$	−2.363
$Mg(OH)_2 + 2H^+ + 2e^- = Mg + 2H_2O$	−1.862
Manganese	
$Mn^{2+} + 2e^- = Mn$	−1.179
$MnO_4^- + e^- = MnO_4^{2-}$	0.564
$MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4OH^-$	0.60
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.228
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.507
$Mn^{3+} + e^- = Mn^{2+}$	1.509
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	1.692
$MnO_4^{2-} + 4H^+ + 2e^- = MnO_2 + 2H_2O$	2.257
Mercury	
$HgS + 2e^- = Hg + S^{2-}$	−0.69
$Hg(CN)_4^{2-} + 2e^- = Hg + 4CN^-$	−0.37
$Hg_2^{2+} + 2e^- = 2Hg$	0.788
$Hg^{2+} + 2e^- = Hg$	0.850
$2Hg^{2+} + 2e^- = Hg_2^{2+}$	0.920

Equation	E°, V
Molybdenum	
$MoO_4^{2-} + 4H_2O + 6e^- = Mo + 8OH^-$	−1.05
$Mo^{3+} + 3e^- = Mo$	−0.200
$MoO_4^{2-} + 8H^+ + 6e^- = Mo + 4H_2O$	0.154
Nickel	
$Ni^{2+} + 2e^- = Ni$	−0.250
$Ni(OH)_3 + e^- = Ni(OH)_2 + OH^-$	0.49
Niobium	
$Nb^{3+} + 3e^- = Nb$	−1.1
$Nb_2O_5 + 10H^+ + 10e^- = 2Nb + 5H_2O$	−0.65
Nitrogen	
$3N_2 + 2e^- = 2N_3^-$	−3.4
$N_2 + 4H_2O + 2e^- = 2NH_2OH + 2OH^-$	−3.04
$N_2 + 4H_2O + 4e^- = N_2H_4 + 4OH^-$	−1.16
$NO_2^- + H_2O + e^- = NO + 2OH^-$	−0.46
$NO_3^- + 2H^+ + e^- = NO_2 + H_2O$	0.78
$NO_3^- + 10H^+ + 8e^- = NH_4^+ + 3H_2O$	0.87
$NO_3^- + 3H^+ + 2e^- = HNO_2 + H_2O$	0.94
$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	0.957
$HNO_2 + H^+ + e^- = NO + H_2O$	0.99
Osmium	
$OsO_4 + 8H^+ + 8e^- = Os + 4H_2O$	0.85
$Os^{2+} + 2e^- = Os$	0.85
Oxygen	
$O_2 + 2H_2O + 4e^- = 4OH^-$	0.401
$O_2 + 2H^+ + 2e^- = H_2O_2$	0.682
$O_2 + 4H^+ + 4e^- = 2H_2O$	1.228
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.776
$O_3 + 2H^+ + 2e^- = O_2 + H_2O$	2.07
Palladium	
$PdI_6^{2-} + 2e^- = PdI_4^{2-} + 2I^-$	0.623
$Pd^{2+} + 2e^- = Pd$	0.987
$PdCl_6^{2-} + 2e^- = PdCl_4^{2-} + 2Cl^-$	1.288
Phosphorus	
$PO_4^{3-} + 2H_2O + 2e^- = HPO_3^{2-} + 3OH^-$	−1.12
$P + 3H_2O + 3e^- = PH_3 + 3OH^-$	−0.89
$H_3PO_4 + 4H^+ + 4e^- = H_3PO_2 + 2H_2O$	−0.39
$H_3PO_4 + 5H^+ + 5e^- = P + 4H_2O$	−0.383
$H_3PO_4 + 2H^+ + 2e^- = H_3PO_3 + H_2O$	−0.276
Platinum	
$Pt^{2+} + 2e^- = Pt$	1.188
Potassium	
$K^+ + e^- = K$	−2.924

Equation	E°, V
Rhenium	
$ReO_4^- + 2H_2O + 3e^- = ReO_2 + 4OH^-$	−0.595
$ReO_4^- + 4H_2O + 7e^- = Re + 8OH^-$	−0.584
$Re^{3+} + 3e^- = Re$	0.3
$ReO_4^- + 8H^+ + 7e^- = Re + 4H_2O$	0.37
Rhodium	
$Rh^{3+} + 3e^- = Rh$	0.8
Rubidium	
$Rb^+ + e^- = Rb$	−2.925
Ruthenium	
$Ru^{2+} + 2e^- = Ru$	0.45
$RuO_2 + 4H^+ + 4e^- = Ru + 2H_2O$	0.79
Selenium	
$Se + 2e^- = Se^{2-}$	−0.92
$Se + 2H^+ + 2e^- = H_2Se$	−0.40
$SeO_3^{2-} + 3H_2O + 4e^- = Se + 6OH^-$	−0.366
$H_2SeO_3 + 4H^+ + 4e^- = Se + 3H_2O$	0.741
$SeO_4^{2-} + 4H^+ + 2e^- = H_2SeO_3 + H_2O$	1.15
Silicon	
$SiO_3^{2-} + 3H_2O + 4e^- = Si + 6OH^-$	−1.7
$SiF_6^{2-} + 4e^- = Si + 6F^-$	−1.2
$SiO_3^{2-} + 6H^+ + 4e^- = Si + 3H_2O$	−0.455
Silver	
$Ag(CN)_2^- + e^- = Ag + 2CN^-$	−0.29
$Ag_2O + H_2O + 2e^- = Ag + 2OH^-$	0.344
$Ag(NH_3)_2^+ + e^- = Ag + 2H_3N$	0.373
$Ag^+ + e^- = Ag$	0.799
Sodium	
$Na^+ + e^- = Na$	−2.714
Sulphur	
$SO_4^{2-} + H_2O + 2e^- = SO_3^{2-} + 2OH^-$	−0.93
$SO_4^{2-} + 4H_2O + 6e^- = S + 8OH^-$	−0.75
$S + 2e^- = S^{2-}$	−0.48
$SO_4^{2-} + 8H^+ + 8e^- = S^{2-} + 4H_2O$	0.149
$S + 2H^+ + 2e^- = H_2S$	0.17
$SO_4^{2-} + 2H^+ + 2e^- = SO_3^{2-} + H_2O$	0.22
$SO_4^{2-} + 8H^+ + 6e^- = S + 4H_2O$	0.357
$S_2O_8^{2-} + 2e^- = 2SO_4^{2-}$	2.010
Strontium	
$Sr^{2+} + 2e^- = Sr$	−2.888
Tantalum	
$Ta_2O_5 + 10H^+ + 10e^- = 2Ta + 5H_2O$	−0.750

Continuation

Equation	E°, V
Technetium	
$Tc^{2+} + 2e^- = Tc$	0.4
$TcO_4^- + 8H^+ + 5e^- = Tc^{2+} + 4H_2O$	0.5
Tellurium	
$Te + 2e^- = Te^{2-}$	−1.14
$Te + 2H^+ + 2e^- = H_2Te$	−0.72
$TeO_3^{2-} + 3H_2O + 4e^- = Te + 6OH^-$	−0.57
$TeO_4^{2-} + 2H^+ + 2e^- = TeO_3^{2-} + H_2O$	0.892
$H_6TeO_6 + 2H^+ + 2e^- = TeO_2 + 4H_2O$	1.02
Thallium	
$Tl^+ + e^- = Tl$	−0.336
$Tl^{3+} + 2e^- = Tl^+$	1.252
Tin	
$Sn(OH)_6^{2-} + 2e^- = HSnO_2^- + 3OH^- + H_2O$	−0.90
$SnF_6^{2-} + 4e^- = Sn + 6F^-$	−0.25
$Sn^{2+} + 2e^- = Sn$	−0.136
$SnO_2 + 4H^+ + 4e^- = Sn + 2H_2O$	−0.106
$Sn^{4+} + 4e^- = Sn$	0.01
$Sn^{4+} + 2e^- = Sn^{2+}$	0.151
Titanium	
$Ti^{2+} + 2e^- = Ti$	−1.630
$Ti^{3+} + 3e^- = Ti$	−1.23
$TiF_6^{2-} + 4e^- = Ti + 6F^-$	−0.19
$TiO^{2+} + 2H^+ + 4e^- = Ti + H_2O$	−0.88
$Ti^{3+} + e^- = Ti^{2+}$	−0.368
$TiO^{2+} + 2H^+ + 5H_2O + e^- = Ti(OH_2)_6^{3+}$	0.1
Tungsten	
$WO_4^{2-} + 4H_2O + 6e^- = W + 6OH^-$	−1.05
$WO_4^{2-} + 8H^+ + 6e^- = W + 4H_2O$	0.049
Vanadium	
$V^{2+} + 2e^- = V$	1.175
$V^{3+} + 3e^- = V$	−0.255
$VO_2^+ + 4H^+ + 5e^- = V + 2H_2O$	−0.25
Zinc	
$Zn(CN)_4^{2-} + 2e^- = Zn + 4CN^-$	−1.26
$Zn^{2+} + 2e^- = Zn$	−0.763
Zirconium	
$ZrO^{2+} + 2H^+ + 4e^- = Zr + H_2O$	−1.570
$Zr^{4+} + 4e^- = Zr$	−1.539
$ZrO_2 + 4H^+ + 4e^- = Zr + 2H_2O$	−1.43
Lanthanides	
$La^{3+} + 3e^- = La$	−2.522
$Ce^{3+} + 3e^- = Ce$	−2.48
$Ce^{4+} + e^- = Ce^{3+}$	1.61
$Pr^{3+} + 3e^- = Pr$	−2.462
$Pm^{3+} + 3e^- = Pm$	−2.423
$Sm^{2+} + 2e^- = Sm$	−3.121
$Eu^{2+} + 2e^- = Eu$	−3.395

Saturated Vapour Pressure of Water at Equilibrium with Water

t, °C	*p*, kPa	*t*, °C	*p*, kPa	*t*, °C	*p*, kPa
10	1.2270	22	2.642	32	4.753
12	1.4014	24	2.982	34	5.318
14	1.597	25	3.166	36	5.940
16	1.817	26	3.360	38	6.623
18	2.062	28	3.778	40	7.374
20	2.337	30	4.241	50	12.334

Preparing Solutions of Wanted Concentration

Ways of expressing concentration of solutions. Per cent concentration: the number of grams of solute dissolved in 100 g of solution.

Molar concentration: the number of moles of solute per litre of solution.

Normality: the number of equivalent weights of solute per litre of solution.

Molar fraction: the number of moles of solute divided by the total number of moles of solvent and solute expressed in fractions of a unity or in per cent.

Examples of calculating solution concentration. 1. What number of grams of sodium hydroxide are required to prepare 2 litres of a 20 per cent solution?

Solution. The density of a 20 per cent solution of NaOH is 1.225 (see the table of densities, Appendix 25). The mass of 2 litres of the solution is

$$m = Vd = 2000 \times 1.225 = 2450 \text{ g}$$

100 g of 20 per cent solution contain 20 g of NaOH

2450 g of 20 per cent solution contain x g of NaOH

$$x = 480 \text{ g NaOH}$$

2. What quantity of water should be added to 200 ml of 68 per cent nitric acid (sp. density, 1.4) to obtain a 10 per cent solution of the acid?

Solution. According to the Table, the density of a 68 per cent solution of nitric acid is 1.4 g/cc. The mass of HNO_3 in 200 ml of 68 per cent solution is

100 g of solution contain 68 g of HNO_3

200×1.4 g of solution contain x g of HNO_3

$$x = 190.4 \text{ g}$$

The same mass of HNO_3 makes 10 per cent of the mass of dilute solution. The mass of 10 per cent solution of HNO_3:

100 g of 10 per cent solution contain 10 g of HNO_3

x g of 10 per cent solution contain 190.4 g of HNO_3

$$x = 1904 \text{ g}$$

The amount of water required to dilute the acid is

$$1904 - 280 = 1624 \text{ g or } 1624 \text{ ml}$$

3. How many millilitres of 96 per cent sulphuric acid (sp. density, 1.84) should be taken to prepare 2 litres of 0.5 *N* solution?

Solution. An equivalent weight of sulphuric acid is 49 g. One litre of 0.5 *N* acid contains 24.5 g and 2 litres—49 g of H_2SO_4.

The mass of 96 per cent solution of sulphuric acid containing 49 g of hydrogen sulphate is:

100 g of solution contain 96 g of H_2SO_4

x g of solution contain 49 g of H_2SO_4

$$x = 51.04 \text{ g}$$

The volume of a 51.04 g of 96 per cent solution of H_2SO_4 is

$$V = \frac{m}{d} = 27.73 \text{ ml}$$

4. Determine the volume of sulphuric acid solution if 400 ml of water are added to 100 ml of 96 per cent sulphuric acid (sp. density, 1.84).

5. What is the percentage of NaOH in 2 *M* solution of alkali (sp. density, 1.08)?

Determining percent concentration of solution by its specific density. Acquaint yourselves with the structure of the hydrometer (Fig. 105) and select a suitable one. (Each hydrometer is intended to measure the density of solutions within a certain range. It is therefore necessary to know the probable density of the solution in question.)

Obtain the test solution from your instructor and place a sample into the volumetric cylinder. Immerse carefully the hydrometer into the liquid.

Read the hydrometer scale. (Ensure that the hydrometer does not touch the cylinder walls.) Raise the hydrometer to 1-2 cm and release it back into the liquid. Read the scale again. Return the liquid back into its mother bottle. Wash the hydrometer.

Consult the table of densities to determine the concentration of the solution.

If the hydrometer reads the value which is not found in the Table of densities, determine the concentration by interpolation, i.e. by finding the intermediate of two multiples. Act as follows.

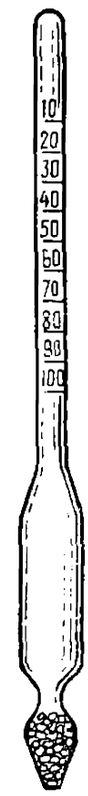


Fig. 105. Hydrometer

Let the hydrometer read the density of a KNO_3 solution of 1.083. The tabulated values of density 1.076 and 1.090 correspond to concentrations of 12 and 14 per cent respectively. Hence, the change in concentration by 2 per cent corresponds to the change in the density of 1.090 — 1.076 = 0.014. The density of the test solution differs from 1.076 by 1.083 — 1.076 = 0.007. Assume that, within a narrow range, the variation of concentration with density is linear and make out the proportion:

$$\begin{matrix} 0.014 - 2\% \\ 0.007 - x \end{matrix} \quad x = 1 \text{ per cent}$$

Hence the concentration of the test solution of KNO_3 is 12 + 1 = 13 per cent.

Note: Hydrometers are normally calibrated at 20 °C. The data in the table are given for this temperature. But the table can be used to determine the concentration of solutions at other temperatures provided high accuracy is not required.

Obtaining solutions of desired concentration by dilution of concentrated solution with water. Follow these instructions:

1. Determine the density of the original solution.
2. Make the requisite calculations.
3. Prepare the required solution by mixing the calculated quantities of the original solution and water.

Appendix 25

Density of Solutions of More Common Mineral Acids and Alkalis in Water at 20° C

Density, g/cc	Concentration, mass %				
	HCl	HNO_3	H_2SO_4	KOH	NaOH
1.000	0.360	0.3296	0.261	0.197	0.159
1.010	2.364	2.164	1.731	1.295	1.04
1.020	4.388	3.982	3.242	2.38	1.94
1.030	6.433	5.784	4.746	3.48	2.84
1.040	8.490	7.530	6.237	4.58	3.74
1.050	10.52	9.259	7.704	5.66	4.65
1.060	12.51	10.97	9.129	6.74	5.56
1.070	14.50	12.65	10.56	7.82	6.47
1.080	16.47	14.31	11.96	8.89	7.38
1.090	18.43	15.95	13.36	9.96	8.28
1.100	20.39	17.58	14.73	11.03	9.19
1.110	22.33	19.19	16.08	12.08	10.10
1.120	24.25	20.79	17.43	13.14	11.01
1.130	26.20	22.38	19.76	14.19	11.92
1.140	28.18	23.94	(20.13)	15.22	12.83
1.150	30.14	25.48	(21.38)	16.26	13.73
1.160	32.14	27.00	(22.62)	17.29	14.64
1.170	34.18	28.51	23.95	18.32	15.54
1.180	36.23	30.00	25.21	19.35	16.44
1.190	38.32	31.47	26.47	20.37	17.34
1.200	—	32.94	27.72	21.38	18.25
1.250	—	40.58	33.82	26.34	22.82
1.300	—	48.42	39.68	31.15	27.41
1.350	—	56.95	45.26	35.82	32.10
1.400	—	66.97	50.50	40.37	36.99
1.450	—	79.43	55.45	44.79	42.07
1.500	—	96.73	60.17	49.10	47.33
1.600	—	—	69.09	—	—
1.700	—	—	77.63	—	—
1.800	—	—	87.69	—	—